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13. ABSTRACT *(Maximum 200 words)*

NMR measurements have been made on polyisobutylene containing gaseous and condensed penetrants (CO_2 and toluene respectively). Both NMR relaxation and pulse field gradient measurements have been made to characterize both penetrant diffusion and polymer segmental motion simultaneously. The relaxation data are analyzed using conventional models for polymer chain dynamics and the diffusion constants are expressed using free volume theories. It is found that there is a correlation between penetrant diffusion and polymer segmental reorientation. This correlation can be quantified both in terms of timescale and free volume requirements. The unusual slow permeability of polyisobutylene to various penetrants can be rationalized. The data provides a very comprehensive base for critical discussion of segmental chain dynamic descriptions and free volume theories in systems of this type.

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MOLECULAR LEVEL CHARACTERIZATION BY NMR OF THE TRANSPORT AND STRUCTURAL ENVIRONMENT OF GASES AND CONDENSED PENETRANTS.

FINAL TECHNICAL REPORT

Paul T. Inglefield.

Sept. 20, 1994.

U.S. Army Reseach Office

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1. Statement of the Problem.

An investigation of the microscopic behaviors of low molecular weight sorbates in polymers is proposed using nuclear magnetic resonance (NMR) spectroscopy. The study will focus on both gases and condensed penetrants. The diffusion of small molecules into polymers has been the subject of many investigations, because of the importance in industrial, medical and biological applications. Some examples are the membrane separation of gases, controlled drug delivery, control of polymerization and the production of barrier materials for packaging and chemical defense. The diffusion of penetrants in polyisobutylene is of special interest since this material displays low permeability for a polymeric rubber above the glass transition. The choices of penetrants are for the gas system, carbon dioxide and for the condensed sysem, toluene.

The purpose of the investigation is to explicitly characterize the molecular details of penetrant transport in terms of the structural and dynamic nature of the sorbed species. From the polymer perpective we also wish to characterize the effect of the sorbed species on the polymer properties, both structural and dynamic. In this regard the effect on the glass transition, sub-glass relaxations and polymer integrity will be important. Also the potential cooperativity between penetrant motion and polymer chain segmental motion will be addressed. The spectroscopic approach here is intended to complement the macroscopic studies by other research groups including those at the Materials Technology Laboratory (Watertown, Ma.) and the Natick Army Laboratory (Natick, Ma.). In a general sense the molecular level approach here will help to develope interpretational models to accommodate both macoscopic and molecular information.

The specific experimental approaches used to characterize both structure and dynamics in these rubber/penetrant systems involve experiments measuring NMR relaxation phenomena and relating those measurements to the molecular motion of the species probed: either polymer or penetrant. This is accomplished using well established motional models for both small molecule reorientation and polymer segmental dynamics. In addition the NMR Pulse Field Gradient technique is used to directly measure the penetrant diffusion constant. This experiment has the advantage of not perturbing the system and the determination is not model dependent. Also any complexity in the diffusion process is revealed (eg heterogenious, anisotropic or restricted diffusion). The timescale during which diffusion is measured, and thus the lengthscale probed, is at the experimenter's control.

Both the temperature and concentration dependence will be measured and interpreted. Current models for molecular dynamics will be combined with the concepts of Free Volume theories to characterize the diffusional behaviours. The comprehensive data base that the relaxation and field gradient measurements yield on all the components simultaneously should provide insight into both the applicability of the theories used and any cooperativity between polymer and penetrant at the local structure level.

2 Participating Scientific Personnel.

Paul T. Inglefield	Principal Investigator
Alan A. Jones	Co-Principal Investigator
Wen-Yang Wen	Co-Principal Investigator
Athinodoros Bandis	Graduate Student M.S. Clark University 1992 Thesis: "Gas Mobility in Glassy Polymers by NMR" Ph.D. Clark University 1994. Thesis: "Molecular Level Characterization and Transport of Penetrants in Rubbery Polymers by NMR"

3. Summary of Results.

The results and conclusions of the project are contained in the following compilation of manuscripts both published and submitted for publication as indicated:

(i) "Nuclear Spin Dynamics of $^{13}CO_2$ Sorbed in Polyisobutylene Rubber" Z.P. Dong, B.J. Cauley, A. Bandis, C.W. Mou, C.E. Inglefield, A.A. Jones, P.T. Inglefield and W.-Y. Wen. J. Polymer Science. Poly. Phys. Ed. 31,1213 (1993).

(ii) "An NMR Study of Segmental Motion in Polyisobutylene and the Relationship to Translational Diffusion of Sorbed CO_2" A. Bandis, W.-Y. Wen, E.B. Jones, P. Kaskan, A.A. Jones, P.T. Inglefield, and J.T. Bendler. J. Polymer Science. Poly. Phys. Ed. 32, 1707 (1994).

(iii) " NMR Study of Segmental Motion in Polyisobutylene and the Relationship to Translational Diffusion of Sorbed CO_2" A. Bandis, W.-Y. Wen, E.B. Jones, P. Kaskan, A.A. Jones and P.T. Inglefield. Polymer Preprints, ACS. 35, 1, 427 (1994)

(iv) "A Nuclear Magnetic Resonance Study of Dynamics in Toluene-Polyisobutylene Solutions: (I) Penetrant Diffusion and Fujita Theory" A. Bandis, P.T. Inglefield, A.A. Jones and W.-Y. Wen. J. Polymer Science. Poly. Phys. Ed. (submitted).

(v) "A Nuclear Magnetic Resonance Study of Dynamics in Toluene-Polyisobutylene Solutions: (II) Ventras-Duda Theory" A. Bandis, P.T. Inglefield, A.A. Jones and W.-Y. Wen. J. Polymer Science. Poly. Phys. Ed. (submitted).

(vi) "A Nuclear Magnetic Resonance Study of Dynamics in Toluene-Polyisobutylene Solutions: (III) Segmental Motion" A. Bandis, P.T. Inglefield, A.A. Jones and W.-Y. Wen. J. Polymer Science. Poly. Phys. Ed. (submitted).

(vii) "A NMR Study of Penetrant Diffusion and Polymer Segmental Dynamics in Rubber" A. Bandis, P.T. Inglefield, A.A. Jones and W.-Y. Wen.

Polymer Materials Sci. and Eng. ACS. 71, 217 (1994)

(viii) "A NMR Study of Penetrant Diffusion and Polymer Segmental Motion in Toluen-Polyisobutylene Solutions" A. Bandis, P.T. Inglefield, A.A. Jones and W.-Y. Wen. ACS Symposium Series, A. Marek, Editor (submitted).

Manuscripts to follow:

Nuclear Spin Relaxation Dynamics of $^{13}CO_2$ Sorbed in Polyisobutene Rubber

Z. P. DONG, B. J. CAULEY, A. BANDIS, C. W. MOU, C. E. INGLEFIELD,
A. A. JONES, P. T. INGLEFIELD, and W.-Y. WEN

Department of Chemistry, Clark University, Worcester, Massachusetts 01610

SYNOPSIS

Recently we presented the dynamics of $^{13}CO_2$ molecules sorbed in silicone rubber (PDMS) ascertained from spin relaxation experiments. Results of a similar investigation for $^{13}CO_2$ sorbed in polyisobutene (PIB) are presented in this report. The spin-lattice and spin-spin relaxation times as well as nuclear Overhauser enhancements (NOE) were determined as a function of temperature and Larmor frequency. The relaxation mechanisms found to be important for $^{13}CO_2$/PIB system are intermolecular dipole-dipole relaxation and chemical shift anisotropy with a minor contribution from spin rotation relaxation. We have determined the parameters which characterize correlation times for $^{13}CO_2$ collisional motion, rotational motion, and translational motions in the PIB. The self-diffusion coefficient of 5.15×10^{-8} cm^2/s obtained from the nuclear magnetic resonance (NMR) data is close to the literature value of the mutual diffusion coefficient of CO_2 in PIB at 300 K obtained from permeability measurements. In contrast to the case of CO_2/PDMS in which a broad distribution (characterized by a fractional exponential correlation function of the Williams-Watts type with $\alpha = 0.58$) is observed, a sharp distribution with a fractional exponent, α, of 0.99 is found for the CO_2/PIB system. Instead of assuming an Arrhenius type temperature dependence, we used a Williams-Landel-Ferry type temperature dependence and found it to be better suited to describe the behavior of this system. PIB is a densely packed "strong" chain polymer which responds gradually to the temperature variation and gas sorption. In contrast PDMS is a relatively loosely packed "fragile" polymer with a propensity to exhibit rapid dynamic responses to the temperature change and gas sorption. © 1993 John Wiley & Sons, Inc.

Keywords: carbon dioxide • spin relaxation • polyisobutylene

INTRODUCTION

Recently we presented a study of the nuclear spin relaxation of sorbed $^{13}CO_2$ in silicone rubber (polydimethyl siloxane).[1] Our analysis showed that the single-mode hypothesis can be used to interpret the experimental spin-lattice relaxation times. However, this hypothesis with a single correlation time was found to be incapable of predicting the nuclear Overhauser enhancements and spin-spin relaxation times. On the other hand, if a distribution of correlation times was assumed, we were able to interpret all of the experimental data in a reasonable manner. We have quantitatively analyzed the spin relaxation mechanisms and determined the parameters which characterize the correlation times for $^{13}CO_2$ collisional motions, rotational motions, and translational motions in the silicone rubber. A fractional exponential correlation function of the Williams-Watts type with a fractional exponent, α, of 0.58 was found in the description of the $^{13}CO_2$ dynamics. This exponent is close to the distribution of time scales associated with segmental motion in the silicone rubber with a value of α in the range of 0.47–0.51.[1]

We have extended our nuclear magnetic resonance (NMR) investigations to another rubbery polymer, polyisobutene (PIB) and determined the spin-lattice relaxation time, T_1, spin-spin relaxation time, T_2, and nuclear Overhauser enhancement

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(NOE) of $^{13}CO_2$ sorbed in the polymer as a function of temperature and Larmor frequency.

Polyisobutene, an elastomer with properties and behavior considerably different from those of silicone rubber, is chosen for our investigations. PIB's wide working range makes it a convenient elastomer for application. Its glass transition temperature (T_g = 205 K) is suitably below the temperature at which the elasticity is desired. It has good chain mobility but not so good that the chains can readily form crystals.[2] PIB is classified as a "strong" chain polymer, while PDMS is considered as one of the "fragile" polymers according to Angell et al.[3] In addition PIB is an elastomer notable for low rates of diffusion of small penetrants.[4] The low diffusion rates have been attributed to efficient intermolecular packing and low total fractional free volume in PIB.[5] Some interesting results we have obtained are reported below. For example, the rotational correlation time at 300 K for CO_2 in PIB is about 800 times longer than that in PDMS. The fractional exponent α is 0.99 for the $^{13}CO_2$/PIB system in contrast to the corresponding value of 0.58 for the $^{13}CO_2$/PDMS system.

EXPERIMENTAL

The polyisobutene sample used for the study was obtained from Cellomer Associates, Inc. of Webster, NY in the form of thick sheets of high-molecular weight (Cat. #40E, Lot #02). The sheets were cut into cylinders 7 mm diameter and 11 mm in length. Four of these cylinders (44 mm in height) were placed in a heavy-wall NMR tube (10 mm o.d. and 1.45 mm wall thickness), then degassed under vacuum for several days. Measured amounts of $^{13}CO_2$ (99.8%, Merck & Co.) were introduced into the NMR tube and the CO_2 pressure was monitored with a transducer-electrometer system. The NMR tube was cooled to the liquid-nitrogen temperature and then sealed. The volume of the PIB sample was 1.69 cm^3 and the volume of the tube above the sample was 3.96 cm^3. The total amount of carbon dioxide in the tube was 2.16×10^{-3} mol and it exerted a pressure of about 10 atm at room temperature. (Concentration of the dissolved $^{13}CO_2$ in PIB was about 1.5% by weight at room temperature.)

Carbon-13 spin-lattice and spin-spin relaxation times (T_1 and T_2) were measured at Larmor frequencies of 22.6, 50.3, and 75.4 MHz on Bruker SXP 20-100, AC-200, and MSL-300 spectrometers, respectively. A simple 180° τ 90° pulse sequence was used to measure T_1 while 90° τ 180° sequence was used to measure T_2. Gated NOE experiments were performed in the AC-200 spectrometer while continuous decoupling was employed on the SXP spectrometer with a decoupler power of 6 or 12 W.

RESULTS

Values of the spin-lattice relaxation time, T_1, for $^{13}CO_2$ sorbed in PIB at various temperatures and a Larmor frequency of 50.3 MHz are presented in Figure 1 as an example. The plot of T_1 versus temperature shows a broad minimum with a T_1 value of 2.9 s at around 290 K. It turns out that the values of T_1 alters only slightly with the change of Larmor frequency in the range 22–75 MHz.

The values of spin-spin relaxation time, T_2, for $^{13}CO_2$ sorbed in PIB at two Larmor frequencies are shown in Figure 2. In contrast to T_1, there is no minimum and the values of T_2 increase rapidly with the increase of temperature. The values of nuclear Overhauser enhancement (NOE) for $^{13}CO_2$ in PIB are plotted as a function of temperature at Larmor frequencies of 22.6 and 50.3 MHz in Figure 3. The NOE values are somewhat scattered but they seem to increase slightly with the temperature and lie in the range 1.06–1.43. Experimental T_1, T_2, and NOE data are summarized and listed in Tables I, II, and III.

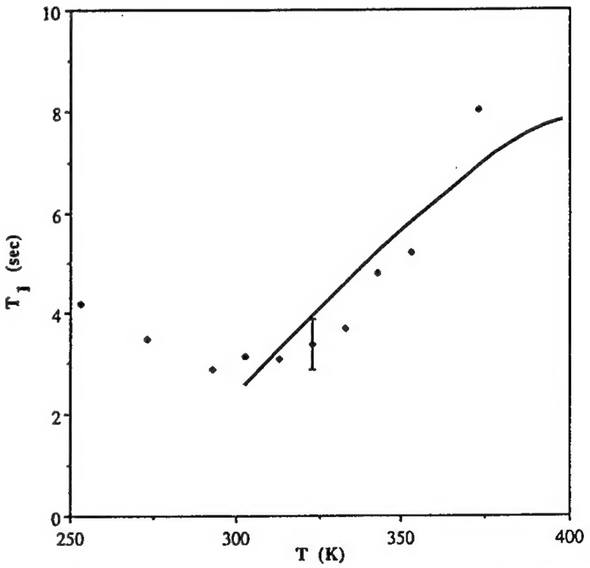

Figure 1. Spin-lattice relaxation time T_1 at 50.3 MHz for $^{13}CO_2$ (10 atm) sorbed in polyisobutene as a function of temperature. The line is a fit based on the Brownian diffusion model for temperatures above T_g (~ 285 K).

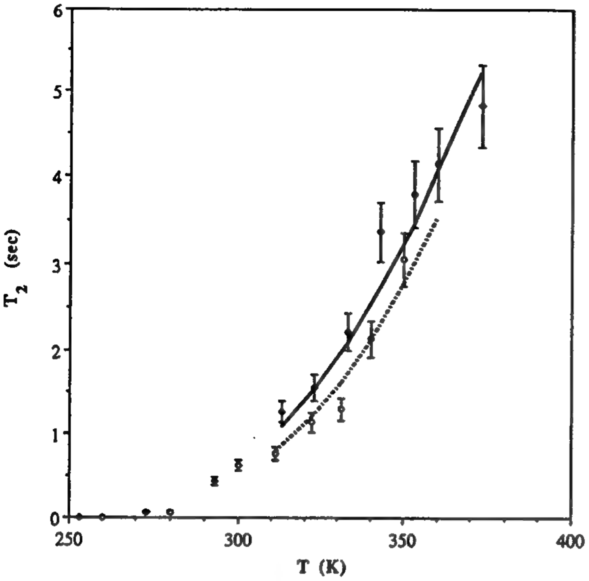

Figure 2. Temperature dependence of T_2 at two Larmor frequencies, 50.3 MHz (♦) and 75.4 MHz (○) for $^{13}CO_2$ (10 atm) sorbed in polyisobutene. The lines are fits based on the Brownian diffusion model for temperatures above T_g (285 ~ 290 K).

Table I. Experimental T_1 and NOE Data for $^{13}CO_2$ (10 atm) Sorbed in Polyisobutene at 22.6 MHz

Temp. (K)	T_1 (s)	NOE
233	—	1.06[a]
253	3.39[a]	1.17[a]
273	3.60[a]	1.21
293	3.04	1.20
313	2.93	1.43
333	4.02	—
353	5.16	—
373	6.09	—

[a] These data are those at temperatures close to or below the glass transition temperature (280 K) of the CO_2/PIB system and, therefore, not used in our model fit to the theory which is applicable to rubbery polymers.

Note: T_g = 205 K + 85 K − 10 K = 280 K.

Interpretation and Analysis

Glass Transition Temperature

The glass transition temperature of PIB as measured by differential scanning calorimetry (DSC) or dynamic mechanical techniques is 205 K. These methods are sensitive to low frequency response (ca. 1 Hz) while the frequencies which are characterized by T_1 are the Larmor frequencies of carbon-13 nuclei and protons, and both of these lie in the mega-Hertz range. We can use the WLF equation to estimate the temperature shift (ΔT_g) associated with the higher frequency of the NMR measurements. Mandelkern[6] has used this approach to characterize the relationship between the glass transition and carbon-13 relaxation for a number of polymers. The actual form of the WLF equation to be employed is

$$\log(\omega_2/\omega_1) = c_1(\Delta T_g)/(c_2 + (\Delta T_g))$$

where c_1 = 16.8 and c_2 = 108.6 K[7] for PIB. For ω_1

Table II. Experimental T_1, T_2, and NOE Data for $^{13}CO_2$ (10 atm) Sorbed in Polyisobutene at 50.3 MHz

Temp. (K)	T_1 (s)	T_2 (s)	NOE
253	4.2[a]	0.004[a]	—
273	3.49[a]	0.070[a]	1.27[a]
293	2.89[a]	0.440[a]	1.14[a]
303	3.13	—	1.12
313	3.10	1.27	1.16
323	3.38	1.55	—
333	3.70	2.21	1.29
343	4.80	3.34	—
353	5.20	3.80	1.33
373	8.04	4.82	—

[a] These data are shown at temperatures close to or below the glass transition temperature (285 K) of the CO_2/PIB system and, therefore, not used in our model fit to the theory which is applicable to rubbery polymers.

Note: T_g = 205 K + 90 K − 10 K = 285 K.

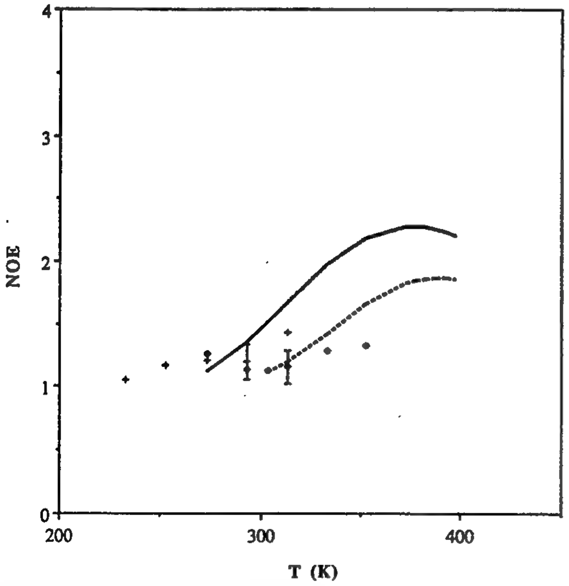

Figure 3. Temperature dependence of NOE at two Larmor frequencies, 22.6 MHz (+) and 50.3 MHz (♦) for $^{13}CO_2$ (10 atm) sorbed in polyisobutene. The lines are fits based on the Brownian diffusion model for temperatures above T_g (280 ~ 285 K).

Table III. Experimental T_1 and T_2 Data for $^{13}CO_2$ (10 atm) Sorbed in Polyisobutene at 75.4 MHz

Temp. (K)	T_1 (s)	T_2 (s)
260	4.62[a]	6.92×10^{-3}[a]
280	—	0.0667[a]
300	1.94[a]	0.635[a]
311	2.93	0.769
322	3.14	1.14
331	3.37	1.30
340	3.96	2.13
350	4.87	3.06
360	5.64	4.14

[a] These data are those at temperatures close to or below the glass transition temperature (290 K) of the CO_2/PIB system and, therefore, not used in our model fit to the theory applicable to rubbery polymers.

Note: $T_g = 205\ \text{K} + 95\ \text{K} - 10\ \text{K} = 290\ \text{K}$.

of 1 Hz and ω_2 in the range 22–75 MHz, the values of ΔT_g fall in the range 85–95 K. This will bring the spin-lattice relaxation estimate of T_g up into the range of 290–300 K.

On the other hand, the glass transition temperature is expected to be lowered by the sorption of CO_2 (10 atm) and the subsequent plasticization of PIB. The depression of T_g by this mechanism is estimated to be about 10 K. A combination of the effects of CO_2 plasticization and the high frequency measurements would bring the T_g into the range 280–290 K for the $^{13}CO_2$/PIB system. This range of the glass transition temperature seems to be consistent with our observations that (a) the T_1 data show a change in slope in the range 290–310 K, (b) the T_2 value decreases suddenly from about 0.5 s to less than 0.1 s when the temperature is lowered from 290 K to 280 K, and (c) as the temperature is raised from 273 to 293 K, the dominant relaxation mechanism of CO_2 changes from CSA to dipole-dipole at a Larmor frequency of 22.6 MHz (see Discussion).

Relaxation Mechanisms

Let us focus our attention on the sources of relaxation for $^{13}CO_2$ above the WLF shifted glass transition in PIB and analyze the experimental data obtained at or above 293 K. Three mechanisms are contributing to the NMR relaxation of $^{13}CO_2$: spin rotation (SR) relaxation, chemical shift anisotropy (CSA) relaxation, and intermolecular dipole-dipole (DD) relaxation. The same equations[1] as used previously to analyze the relaxation of $^{13}CO_2$ sorbed in silicone rubber are applied to study the relaxation for $^{13}CO_2$ in PIB. In addition to assuming the Arrhenius type temperature dependence, we also employ the WLF type temperature dependence for correlation times.

$$\log[\tau(T)/\tau(T_o)] = c_1^o(T - T_o)/(c_2^o + T - T_o) \quad (1)$$

where $T_o = 298$ K, $c_1^o = 8.61$, and $c_2^o = 200.4$ K.[8] Instead of fixing c_1^o as a constant, we treat c_1^o as an adjustable parameter and let it play a role similar to ΔH, the energy of activation in the Arrhenius type equation.

In the previous study of $^{13}CO_2$ in silicone rubber, it was necessary to assume the distribution of dynamical CO_2 motions.[1] We shall also use the Williams-Watts type correlation function to depict motion of CO_2 in PIB:

$$\phi(t) = \exp[-(t/\tau_p)^{\alpha}] \quad (2)$$

In eq. (2), τ_p is the central correlation time and sets the position of the distribution on the time axis. The parameter α, which falls in the range of $0 < \alpha \leq 1$, determines the width of the distribution.

There are a total of 37 data points and our model contains at least six potentially adjustable parameters. They are correlation times $\tau_{SR}(300\ \text{K})$, τ_{CSA} (300 K), and τ_{DD} (300 K) for spin rotation, chemical shift anisotropy, and dipole-dipole interaction, respectively; width parameter for distribution (α), distance of closest approach for CO_2 to PIB protons (b), and either the WLF parameter (c_1^o) or the Arrhenius activation energy (ΔH).

The fitting procedure now comes into play and the values of T_1, T_2, and NOE computed by the equations[1] are compared with the experimental values. Then the values of the six adjustable parameters are changed in an effort to minimize the sum of squares (the least squares).

The Best Fit Results

The resulting fit has root-mean-square residuals of 11%, which is also the approximate value of our experimental error. The results of the fits for the T_1, T_2, and NOE data are shown in Figures 1, 2, and 3, respectively. Note that in all cases the fits are for the rubbery regime above T_g only. The parameters of the best fit are:

$$\tau_{SR}(300\ \text{K}) = 2.9 \times 10^{-15}\ \text{s}$$

$$\tau_{CSA}(300\ \text{K}) = 1.3 \times 10^{-10}\ \text{s}$$

$$\tau_{DD}(300\ \mathrm{K}) = 2.6 \times 10^{-8}\ \mathrm{s}$$

$$\alpha = 0.99$$

$$c_1^g = 8.6; \quad \Delta H = 28.2\ \mathrm{kJ/mol}$$

$$b = 3.66 \times 10^{-8}\ \mathrm{cm}$$

Since the distance of the closest approach for carbon-13 of $^{13}CO_2$ to PIB protons can be estimated from the van der Waals radii and the result is close to the above value, b can be eliminated and no longer considered as an adjustable parameter. The WLF parameter c_1^g determined by the fitting process turns out to be 8.6, which is practically identical to the literature value[8] and therefore it can be eliminated also. The remaining parameters are just four: three τ's and α.

DISCUSSION

The overall relaxation rate at each temperature and Larmor frequency is a sum of the rates from three mechanisms:

$$1/T_1 = 1/T_1(\mathrm{CSA}) + 1/T_1(\mathrm{DD}) + 1/T_1(\mathrm{SR}) \quad (3)$$

In order to see the contributions of each mechanism to the overall relaxation, calculated values of the rates, $1/T_1(\mathrm{CSA})$, $1/T_1(\mathrm{DD})$, and $1/T_1(\mathrm{SR})$ are plotted in Figures 4, 5, and 6, respectively, as functions of temperature at three Larmor frequencies. Though our calculations are based on the experimental data for $^{13}CO_2$ in rubbery PIB in the temperature range 303–373 K, we have expanded the range of our plots to cover a wider temperature range

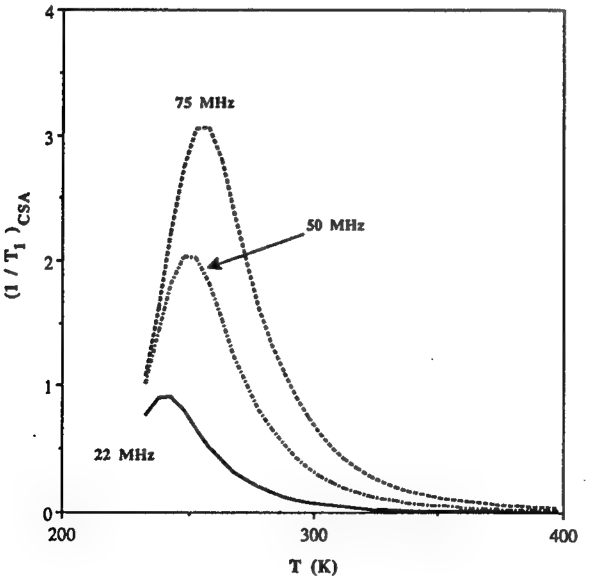

Figure 4. The chemical shift anisotropy contribution to the spin-lattice relaxation rate at three Larmor frequencies, 22.6 MHz (——), 50.3 MHz (– • –), and 75.4 MHz (– – –) as a function of temperature.

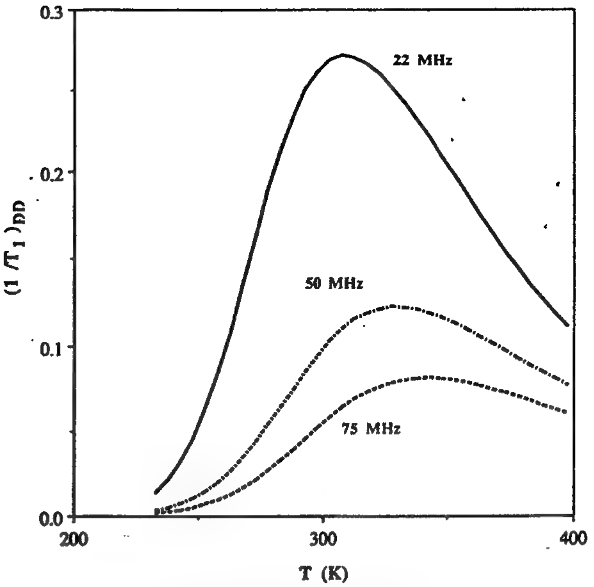

Figure 5. The dipole-dipole interaction contribution to the spin-lattice relaxation rate at three Larmor frequencies, 22.6 MHz (——), 50.3 MHz (– • –), and 75.4 MHz (– – –) as a function of temperature.

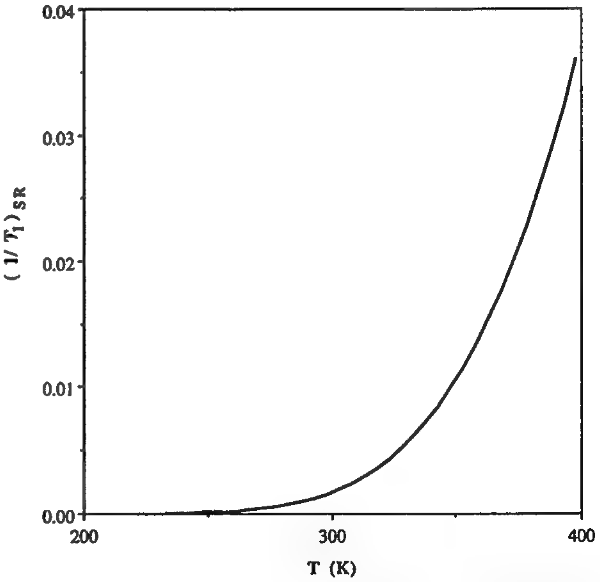

Figure 6. The spin rotation contribution to the spin-lattice relaxation rate as a function of temperature. $T_1(\mathrm{SR})$ is independent of Larmor frequency.

Table IV. Contributions of the Chemical Shift Anisotropy Mechanism to the Overall Spin-Lattice Relaxation of $^{13}CO_2$ Sorbed in Rubbery Polyisobutene

	22.6 MHz		50.3 MHz		75.4 MHz	
Temp (K)	T_1 (CSA) (s)	Percent of Total	T_1 (CSA) (s)	Percent of Total	T_1 (CSA) (s)	Percent of Total
233	1.31	98	0.99	99.7	0.93	99.9
253	1.52	91	0.50	99	0.33	99.8
273	4.01	61	1.00	96	0.51	99
293	10.7	27	2.32	83	1.10	95
313	25.9	12	5.32	61	2.40	85
333	54.9	6.8	11.2	41	4.96	70
353	104	4.4	21.1	27	9.36	54
373	181	3.1	36.7	19	16.2	40
393	293	2.2	59.4	13	26.3	29

233–393 K for the purpose of seeing some features of interest which may be taking place at or slightly below the spin-lattice relaxation estimate of T_g (280–290 K). The estimated percent contributions are listed in Tables IV, V, and VI, and also plotted in Figure 7 as a function of temperature at 22.6 MHz.

As can be seen from Figure 7, the CSA and DD contributions to the spin-lattice relaxation are substantial and change greatly as a function of temperature in the range 250–330 K. As the temperature increases, the dominant mechanism alters from CSA to DD, and the two curves (%CSA vs T and %DD vs T) cross each other at around 280 K, which is the glass transition temperature for the $^{13}CO_2$/PIB system at the Larmor frequency of 22.6 MHz. For CO_2 sorbed in glassy polycarbonate and glassy polystyrene, the dominant relaxation mechanism is CSA. The drop in the contribution of this mechanism at around 280 K in PIB is further evidence of the change from glassy behavior to rubbery behavior at the frequency of the NMR experiment.

For comparison with CO_2 in another rubbery polymer, we show the percent contributions of each mechanism to the spin-lattice relaxation for $^{13}CO_2$/PDMS system[1] at 22.6 MHz in Figure 8. In the PDMS case, the CSA mechanism is a very minor contribution, which is consistent with a rubbery system. The dominant mechanisms for CO_2 in PDMS are SR and DD, and their contributions change only slightly with the temperature. It should be pointed out that the temperature range of our interest, 230–390 K, is considerably above the spin-lattice relaxation time view of T_g (192 K) for $^{13}CO_2$/PDMS system at 22.6 MHz. The weak temperature

Table V. Contributions of the Dipole-Dipole Mechanism to the Overall Spin-Lattice Relaxation of $^{13}CO_2$ Sorbed in Rubbery Polyisobutene

	22.6 MHz		50.3 MHz		75.4 MHz	
Temp (K)	T_1 (DD) (s)	Percent of Total	T_1 (DD) (s)	Percent of Total	T_1 (DD) (s)	Percent of Total
233	74.9	1.7	354	0.3	786	0.09
253	15.9	8.7	69.1	0.7	149	0.2
273	6.16	39	22.8	4.2	46.4	1
293	4.00	73	11.7	16	21.8	5
313	3.70	87	8.70	38	14.5	14
333	4.13	91	8.20	56	12.4	28
353	5.06	90	8.87	66	12.5	40
373	6.49	86	10.3	67	13.8	47
393	8.47	77	12.4	62	15.9	47

Table VI. Contributions of the Spin Rotation Mechanism to the Overall Spin-Lattice Relaxation of $^{13}CO_2$ Sorbed in Rubbery Polyisobutene

		% Contribution of the Spin Rotation Mechanism		
Temp (K)	T_1 (SR) (s)[a]	22.6 MHz	50.3 MHz	75.4 MHz
233	60040	0	0	0
253	10260	0	0	0
273	2602	0.1	0	0
293	868	0.3	0.2	0.1
313	352	0.9	1.0	0.6
333	166	2.3	2.8	2
353	87.3	5.2	6.4	6
373	50.2	11.1	14	13
393	31.0	21.0	25	24

[a] Calculated spin-lattice relaxation times due to the spin-rotation mechanism. T_1 (SR) is independent of the Larmor frequency.

dependence is consistent with the "WLF behavior" at temperatures well above T_g. The importance of the SR mechanism in PDMS relative to PIB is also an indication of greater mobility in the lower T_g material.

A distribution of CO_2 motions in the silicone rubber was observed and characterized by a fractional exponential correlation function of the Williams-Watts type with a fractional exponent, α, of 0.58.[1] In contrast, the distribution of CO_2 motions in PIB must be very narrow since the value of the width parameter α is 0.99. Consequently the population distribution of the self-diffusion coefficient, D, for CO_2 sorbed in PIB will also be very narrow. The mean value of D at 300 K is given by

$$\langle D \rangle = b^2/\langle \tau_{DD} \rangle = 5.15 \times 10^{-8}\ \mathrm{cm^2/s} \qquad (4)$$

which is close to the mutual diffusion coefficient of 5.78×10^{-8} cm²/s reported by Van Amerongen[4]

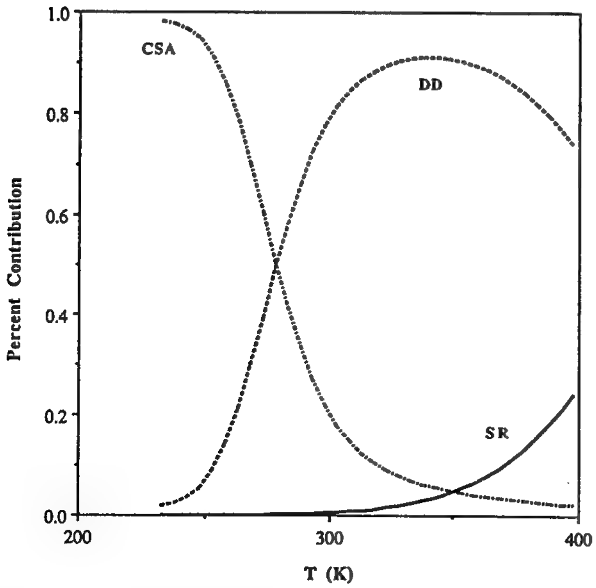

Figure 7. Percent contributions of CSA, DD, and SR mechanisms at 22.6 MHz for $^{13}CO_2$ (10 atm) sorbed in polyisobutene as a function of temperature.

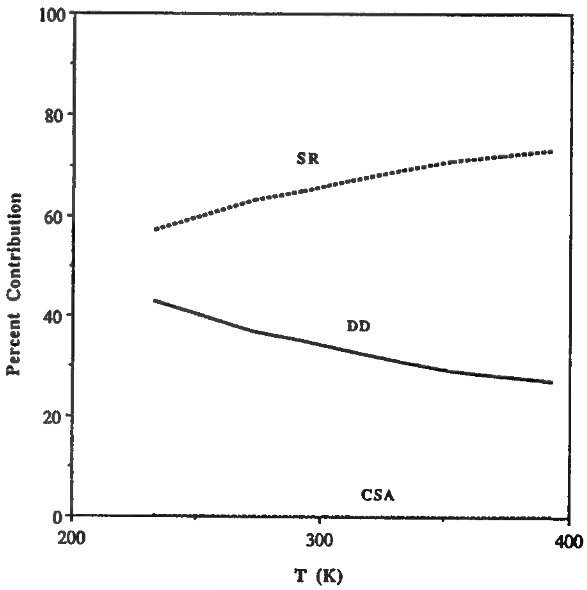

Figure 8. Percent contributions of CSA, DD, and SR mechanisms at 22.6 MHz for $^{13}CO_2$ (10 atm) sorbed in silicone rubber as a function of temperature.

from his permeability measurements of CO_2 sorbed in PIB. Given the complexity of the interpretation of the NMR data and the short-range viewpoint of the NMR experiment, the agreement is better than should be expected.

Good agreement between the NMR results and permeability results was also obtained from the interpretation of the PDMS system. This lends some credibility to the connections between the dynamics determined from NMR and from permeability data.

With regard to the spin rotation, the correlation time τ_{SR} for CO_2 in PIB is 2.9×10^{-15} s which is smaller by a factor of 30 than the corresponding value of 8.8×10^{-14} s in PDMS. This is explicable in terms of the number of collisions suffered by CO_2 molecules in these polymers: it is much greater in PIB than in PDMS, since the former is a much more tightly packed polymer than the latter.[5] Next, the value of τ_{CSA} is 1.3×10^{-10} s in PIB which may be compared with the corresponding value of 1.6×10^{-13} s at 300 K in PDMS. The fact that the rotational correlation time is almost three orders of magnitude greater in PIB than in PDMS can also be attributed to the tighter packing of the former than the latter.[9]

If an Arrhenius fit is used, the energy of activation ΔH for CO_2 in PIB is found to be 28 kJ/mol which is considerably greater than the corresponding value of only 1.6 kJ/mol in PDMS. Qualitatively this difference is in the direction to be expected, but quantitatively the difference is extremely large. It seems to require re-examination of the meaning of the activation energy for diffusion of sorbed CO_2 in polymers. Since a rubbery polymer is known to follow the WLF equation[8] and not the Arrhenius type equation, the value of ΔH estimated is expected to change with the temperature of observation. In other words, ΔH is a function of temperature T, but more correctly, it is a function of T/T_g where T_g is the glass transition temperature of CO_2/polymer system. If the temperature T is 300 K and the Larmor frequency is 22.6 MHz, then the values of T/T_g are 1.07 and 1.56 for CO_2/PIB and CO_2/PDMS, respectively. At 300 K, the CO_2/PIB system is, therefore, much closer to T_g than the CO_2/PDMS system. The value of ΔH near glass transition (CO_2/PIB case) would be much greater than that at temperature far above the glass transition (CO_2/PDMS case) in agreement with our observation.

In the fitting process, the best result is obtained with the value of α nearly equal to 1, though the quality of the fit changes little as α is varied from 0.8 to 1.0. For this very narrow distribution, eq. (4) is accurate but it does not apply to the PDMS system where a broad distribution is in effect. For silicone rubber at 300 K we have

$$\langle \tau_{DD} \rangle = 7.8 \times 10^{-7}\ \text{s} \quad \text{and} \quad \langle D \rangle = 1.8 \times 10^{-5}\ \text{cm}^2/\text{s}. \qquad (5)$$

Note that $\langle \tau_{DD} \rangle$ for PIB is a factor of 30 smaller but $\langle D \rangle$ is a factor of 350 smaller. It is the effect of the distribution of correlation times in PDMS which leads to the relatively high permeability in that system.

The time scale of segmental motion in PDMS at 300 K is 2×10^{-13} s based on an interpretation of proton spin relaxation data using a Williams-Watts stretched exponential correlation function with an exponent of 0.47.[10] A preliminary measurement of carbon-13 T_1 data on PIB shows a T_1 minimum at slightly above room temperature and at a Larmor frequency of 75 MHz. This corresponds to a correlation time of about 2×10^{-9} s. Thus for PIB, τ_{DD} for CO_2 is within an order of magnitude of the correlation time for segmental motion. This approximate coincidence would indicate a possible relationship; namely, the backbone motion of the PIB gates the translational diffusion of the CO_2. In PDMS, the τ_{DD} for CO_2 is 6 orders of magnitude larger than the correlation time for segmental motions indicating a substantially different relationship between segmental motion and translational diffusion of the sorbed CO_2. A more definitive correlation of polymer motions and penetrant motions will be left for future considerations. The position of the T_1 minimum in PIB is very close to the shift in temperature estimated from the WLF equation. It should also be noted that the temperature at which carbon-13 spectra can no longer be resolved under conditions of simple scalar decoupling is only also slightly lower than the temperature of the T_1 minimum. The proximity of the minimum and the temperature at which scalar decoupling fails to produce resolution is especially close in PIB and reflects the unusual WLF parameter associated with this polymer.[6]

This behavior of the two contrasting polymer systems, PIB and PDMS, may be considered in the context of the description developed by Angell et al.[3] In the CO_2/PDMS system, CO_2 molecules probe the dynamics of the "fragile" polymer with a broad distribution. In the CO_2/PIB system, on the other hand, CO_2 molecules probe the "strong" polymer with a narrow distribution of correlation times. PIB is a densely packed polymer with a small total free volume,[5] and responds gradually to the temperature variation and gas sorption. In contrast, PDMS is a relatively loosely packed polymer with a propensity to exhibit rapid dynamic response to gas sorption and temperature change.

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An NMR Study of Segmental Motion in Poly(isobutylene) and the Relationship to Translational Diffusion of Sorbed CO_2

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SYNOPSIS

The spin-lattice relaxation times as well as nuclear Overhauser enhancements (NOE) are determined for the methylene carbon of polyisobutylene (PIB). Three different correlation functions are used to treat the relaxation data to describe the local motion of the PIB backbone rubber. The first is the Hall–Helfand function combined with restricted anisotropic rotational diffusion, the second is the Dejean–Lauprêtre–Monnerie function, and the third is the Williams–Watts function combined with restricted anisotropic rotational diffusion. Spin-lattice relaxation times are also determined on PIB under pressure of CO_2 gas to check for changes in segmental motion in the presence of this penetrant. All the models give a satisfactory description for the local dynamics of the backbone carbon of the polymer chain, yielding comparable values for the time scale of conformational changes, apparent activation energies and distribution of correlation times. In addition, a proton line shape experiment is performed on bulk PIB as a function of temperature. The results are interpreted in terms of two motional components in the polymer chains: fast and slow ones. Applying a revised version of Rössler's formalism to our data, an average energy barrier is found which is consistent with the apparent activation energies. The apparent activation energy obtained for PIB, from the nuclear magnetic resonance (NMR) measurements, about 35 kJ, is slightly higher than the apparent activation energy for the translational diffusion of CO_2 in PIB from NMR data. The distribution of correlation times and the correlation times themselves for segmental motion of the PIB and translational diffusion of CO_2 in PIB are very similar, indicating a close link between the two motional processes. The distribution of correlation times is close to a single exponential in PIB consistent with Angell characterization of this material as a strong liquid. © 1994 John Wiley & Sons, Inc.

Keywords: polyisobutylene • chain dynamics • gas diffusion

INTRODUCTION

As a polymeric rubber, poly(isobutylene) (PIB) is quite different from nearly all other such systems and therefore has been the subject of ongoing interest. From a traditional standpoint, the Williams–Landel–Ferry (WLF) parameters for time–temperature superposition are unusual.[1] The values correspond to a slow increase in segmental motion above the glass transition. In the Angell classification,[2] PIB is a strong liquid. Thus the slow increase of the time scale of motion above the glass transition is closer to an Arrhenius temperature dependence than most other polymers. Also such strong systems typically display a narrower distribution of correlation times. The segmental motion in this polymer is thought to be sterically hindered even though the glass transition temperature is quite low. The polymer has a low permeability to gases which is typically associated with the low specific volume in this system. Molecular packing has been investigated by Boyd[3-5] using Monte Carlo techniques; these authors

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also investigated penetrant diffusion using molecular dynamics simulations.

In a previous nuclear magnetic resonance (NMR) study,[6] the time scale of translational diffusion of CO_2 in PIB on a local scale was observed to be close to the time scale of the segmental motion of the polymer. The objective of this report is to more carefully characterize the time scales of segmental motion in PIB using NMR spectroscopy so any link to the time scale of penetrant diffusion will be clearer. The Kohlrausch-Williams-Watts or stretched exponential was used to characterize the distribution of translational correlation times for the CO_2 and it was found to be quite narrow. Comparable information on the segmental motion of the polymer itself appeared to be not readily available, lending additional motivation for this study. Based on the strong liquid characterization, a narrow distribution of segmental correlation times would however be expected.[2]

Dejean et al.[7] have used carbon-13 T_1 and NOE measurements at two Larmor frequencies to determine the time scale of segmental motion which is a well-established technique for polymers above the glass transition temperature. However the stretched exponential was not used in the interpretation. Rather than reinterpret these data, new measurements were performed at three Larmor frequencies to extend the database. Several correlation functions are employed in this report to interpret the new data so that the effect of the interpretational model on the time scale and temperature dependence of the motion can be seen.

In addition some relaxation measurements were performed on PIB under a pressure of CO_2 comparable to that employed in the study of CO_2 dynamics to check for alteration of the segmental motion of the polymer in the presence of the gas. Stuk[8] has made predictions concerning the effect of a gaseous penetrant on the segmental motion in a rubbery polymer.

With these new measurements and the associated interpretation, a more accurate comparison of the time scale of segmental motion can be made with the time scale of translational diffusion of the CO_2 in the polymer.

EXPERIMENTAL

The polyisobutylene sample used for the study was obtained from Cellomer Associates, Inc. of Webster, NY in the form of thick sheets of high molecular weight (Cat. #40E, Lot #02, m.wt 1,000,000). NMR experiments were carried out on Bruker SXP (20–100), AC-200 and MSL-300 spectrometers, which correspond to 22.6 MHz, 50.3 MHz and 75.5 MHz ^{13}C Larmor frequencies, respectively. The measurements on the PIB in the PIB–CO_2 system were made on the AC 200.

A simple 180-τ-90° pulse sequence was used to measure the spin-lattice relaxation time (T_1). Gated NOE experiments were performed on the AC-200 and on the SXP (20–100). High power decoupling was used for the T_1 measurements on the MSL-300 and broadband scalar decoupling on the AC-200 and SXP (20–100). Two to three hours have been allowed for the sample to reach a thermal equilibrium before each measurement.

Proton line shape experiments were performed on the MSL-300 using a solid echo sequence (90–τ-90°).

RESULTS

Values of T_1 and the NOE for the methylene carbon in PIB, at various temperatures and Larmor frequencies are presented in Figures 1 and 2. As can be seen from the figures the T_1 minimum is shifted to higher temperatures as the field strength is increased[9] in agreement with expectations. Figure 1 also shows T_1 as a function of temperature for the methylene carbon in PIB in the PIB-CO_2 system.

Experimental and theoretical line shape spectra are shown in Figure 3. Figure 4 shows the mobile population of pure PIB as a function of temperature.

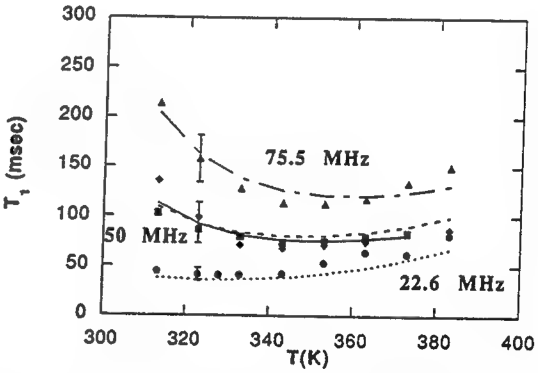

Figure 1. T_1 vs. temperature at 22.6, 50.3, and 75.5 MHz. Lines correspond to the fit for the DLM autocorrelation function. Fits from the other models are comparable to the fit shown for the DLM model. Squares show the T_1 vs. temperature at 50.3 MHz for the PIB-CO_2 system. The solid line corresponds to the fit for the Williams-Watts function combined with anisotropic restricted rotational diffusion.

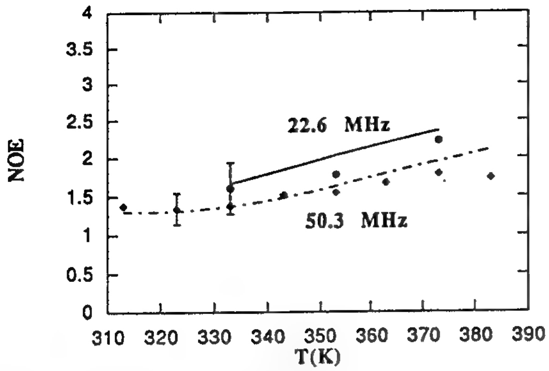

Figure 2. NOE vs. temperature at 22.6 and 50.3 MHz. Lines correspond to the fit for the DLM autocorrelation function. Fits from other models are comparable to the fit shown for the DLM model.

INTERPRETATION

The equations relating the spin-lattice relaxation time and the spectral densities $J(\omega)$ for a methylene carbon-13 nucleus are:

$$\frac{1}{T_1} = W_0 + 2W_{1C} + W_2$$

$$W_0 = \sum_j \gamma_C^2\gamma_H^2\left(\frac{h}{2\pi}\right)^2 \frac{J_0(\omega_0)}{20r_j^6} \qquad \omega_0 = \omega_H - \omega_C$$

$$W_{1C} = \sum_j 3\gamma_C^2\gamma_H^2\left(\frac{h}{2\pi}\right)^2 \frac{J_1(\omega_C)}{40r_j^6}$$

$$W_H = \sum_j 3\gamma_H^2\gamma_C^2\left(\frac{h}{2\pi}\right)^2 \frac{J_2(\omega_2)}{10r_j^6} \qquad \omega_2 = \omega_H + \omega_C$$

The equation for the NOE is given by:

$$\text{NOE} = 1 + \frac{\gamma_H}{\gamma_C}\frac{6J_2(\omega_2) - J_0(\omega_0)}{J_0(\omega_0) + 3J_1(\omega_C) + 6J_2(\omega_2)}$$

$$\omega_0 = \omega_H - \omega_C \quad \omega_2 = \omega_H + \omega_C$$

The methylene C—H distance is known from previous studies to be 1.09 Å.

A number of expressions for the spectral density function or alternatively the correlation function have been developed for segmental motion of the polymer.

One of them is the Hall-Helfand[10] model combined with anisotropic restricted rotational diffusion.[11–14] The spectral density function is shown below:

$$\begin{aligned} J(\omega) = \Bigg\{ & A + \frac{B}{l^2}[(1 - \cos l)^2 + \sin^2 l] \\ & + \frac{C}{4l^2}[(1 - \cos 2l)^2 + \sin^2 2l]\Bigg\} J^{01}(\omega) + \frac{B}{2} \\ & \times \sum_{n=1}^{\infty}\left[\left(\frac{1 - \cos(l - n\pi)}{l - n\pi} + \frac{1 - \cos(l + n\pi)}{l + n\pi}\right)^2\right. \\ & \left. + \left(\frac{\sin(l - n\pi)}{l - n\pi} + \frac{\sin(l + n\pi)}{l + n\pi}\right)^2\right] J^{\lambda_n}(\omega) + \frac{C}{2} \\ & \times \sum_{n=1}^{\infty}\left[\left(\frac{1 - \cos(2l - n\pi)}{2l - n\pi} + \frac{1 - \cos(2l + n\pi)}{2l + n\pi}\right)^2\right. \\ & \left. + \left(\frac{\sin(2l - n\pi)}{2l - n\pi} + \frac{\sin(2l + n\pi)}{2l + n\pi}\right)^2\right] J^{\lambda_n}(\omega) \end{aligned}$$

where

$$\begin{aligned} J^{01}(\omega) = 2\{ & [\tau_0^{-1}(\tau_{01}^{-1} + \tau_1^{-1}) - \omega^2]^2 \\ & + [2\tau_{01}^{-1}\omega]^2\}^{-1/4} \\ & \times \cos\left[\frac{1}{2}\tan^{-1}\frac{2\tau_{01}^{-1}\omega}{\tau_0^{-1}(\tau_{01}^{-1} + \tau_1^{-1}) - \omega^2}\right] \end{aligned}$$

$$\begin{aligned} J^{\lambda_n}(\omega) = 2\{ & [(\tau_0^{-1} + \lambda_n)(\tau_{01}^{-1} + \tau_1^{-1} + \lambda_n) - \omega^2]^2 \\ & + [2(\tau_{01}^{-1} + \lambda_n)\omega]^2\}^{-1/4} \\ & \times \cos\left[\frac{1}{2}\tan^{-1}\frac{2(\tau_{01}^{-1} + \lambda_n)\omega}{(\tau_0^{-1} + \lambda_n)(\tau_{01}^{-1} + \tau_1^{-1} + \lambda_n) - \omega^2}\right] \end{aligned}$$

where

$$\tau_{01}^{-1} = \tau_0^{-1} + \tau_1^{-1} \quad \lambda_n = \left(\frac{n\pi}{l}\right)^2 D_{ir}$$

and

$$A = \tfrac{1}{4}(3\cos^2\Delta - 1)^2 \quad B = \tfrac{3}{4}(\sin^2 2\Delta)$$
$$C = \tfrac{3}{4}(\sin^4\Delta) \tag{1}$$

The angle Δ is between the internuclear vector and the axis of rotation, the latter being the carbon–carbon backbone bonds for this case.

In this description, the time scale of the segmental motion is set by two parameters: τ_0, the correlation time for single conformational transitions and τ_1, the correlation time for cooperative or correlated transitions. Other parameters used, are the activation energies for the above correlation times (τ_0, τ_1) E_{a0} and E_{a1}, respectively, the angular amplitude over which rotational diffusion occurs, l, and the rota-

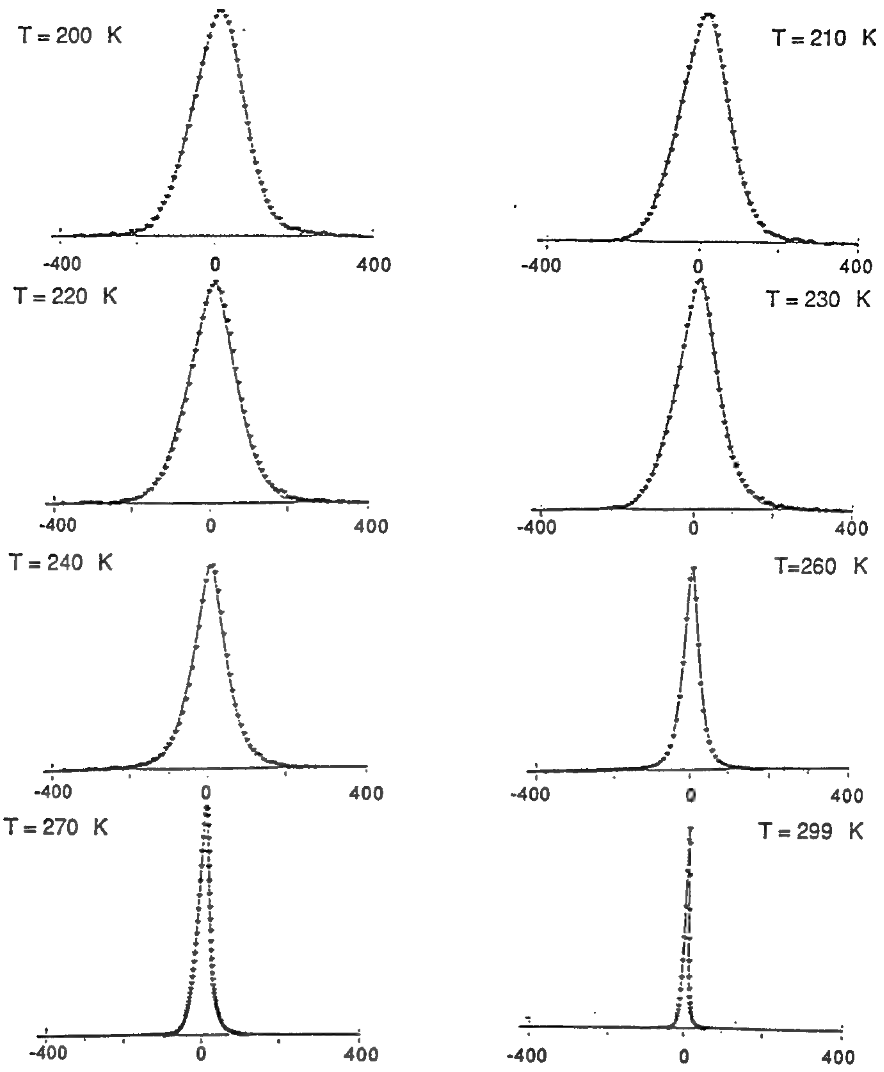

Figure 3. Proton line shapes for neat PIB; all the scales are in ppm.

tional diffusion constant D_{ir}. An Arrhenius temperature dependence was given to the correlation times (τ_0, τ_1) and the temperature dependence of the restricted diffusion[12] (following Gronski's example) is

$$l = AT^{0.5}\ (\text{deg})$$

$$D_{ir} = BT - C\ (\text{s}^{-1})$$

The preceding spectral density function gave a satisfactory fitting based on the following parameters:

$$l = 5.15T^{0.5}\ (\text{deg})$$

$$D_{ir} = 3.26 \times 10^7 T - 3.5 \times 10^9\ (\text{s}^{-1})$$

$$\tau_0 = (\tau_\infty)_0 \exp(E_{ao}/RT) \quad \tau_1 = (\tau_\infty)_1 \exp(E_{a1}/RT)$$

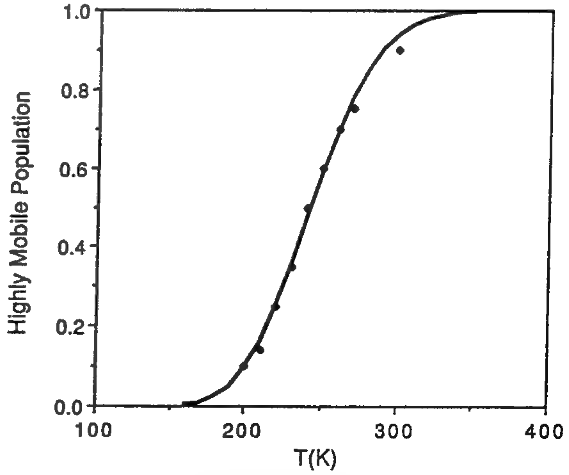

Figure 4. Fraction of highly mobile population for bulk PIB as a function of temperature.

where

$$(\tau_\infty)_0 = 2.1 \times 10^{-14}\ \mathrm{s} \quad (\tau_\infty)_1 = 1.0 \times 10^{-14}\ \mathrm{s}$$

$$E_{a0} = 36.2\ \mathrm{kJ/mole} \quad E_{a1} = 36.7\ \mathrm{kJ/mole}$$

The reasonable fits are obtained for activation energies varying between 29 to 37 kJ/mole and the uncertainties for $(\tau_\infty)_0$, $(\tau_\infty)_1$, are a factor of 5. The uncertainty in l is about 10 degrees and for D_{ir} is about 30 $10^8\ \mathrm{s}^{-1}$.

The data were also fitted using a WLF temperature dependence for the correlation times instead of an Arrhenius dependence:

$$\log_{10}\frac{\tau(T)}{\tau(T_0)} = \frac{-c_1^0(T-T_0)}{c_2^0+T-T_0}$$

where[1] $T_0 = 298$ K and $c_2^0 = 200.4$ K while c_1^0 and $\tau(T_0)$ were floated. This time an acceptable fitting was obtained for the following parameters:

$$\tau_0(298\ \mathrm{K}) = 5.4\ 10^{-8}\ \mathrm{s}$$

$$\tau_1(298\ \mathrm{K}) = 3.4\ 10^{-8}\ \mathrm{s}$$

$$l = 5.4T^{0.5}\ (\mathrm{deg})$$

$$D_{ir} = 2.1 \times 10^7 T\ (\mathrm{s}^{-1})$$

$$c_1^0 = 5$$

The quality of the fitting is the same as the one with an Arrhenius temperature dependence presented before. The uncertainty of the c_1^0 is about 0.3 and the uncertainties of the other parameters are approximately the same as before (Arrhenius fitting).

A different spectral density function was also used to fit the data. This is the Dejean-Lauprêtre-Monnerie (DLM) function(7) [15–17]. The autocorrelation function is:

$$G(t) = (1-a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) + a\exp(-t/\tau_0)$$

where I_0 is the modified Bessel function of order zero and

$$1 - a = \left[\frac{\cos\theta - \cos^3\theta}{2(1-\cos\theta)}\right]^2$$

where θ is a cone half-angle in which random anisotropic reorientation of the CH vector occurs.[18] In this model the local chain motion consists of conformational jumps and bond libration. The development of this correlation function was in response to the realization of the importance of librational motion as a source of spin-lattice relaxation in rubbery systems and the inclusion of librational motion in the other correlation functions reflects this finding by Dejean, Lauprêtre, and Monnerie.[15–17] The correlation time τ_1 is associated with correlated jumps responsible for orientation diffusion along the chain and τ_2 corresponds to damping which consists either of nonpropagative specific motions or of distortions of the chain with respect to its most stable local conformations. τ_0 is associated with the local anisotropic reorientation, i.e. libration. The spectral density function is given by:

$$J(\omega) = \mathrm{Re}\left(\frac{1-a}{(\alpha+i\beta)^{1/2}} + \frac{a\tau_0}{1+\omega^2\tau_0^2}\right) \tag{2}$$

where

$$\alpha = \tau_2^{-2} + 2\tau_1^{-1}\tau_2^{-1} - \omega^2 \quad \beta = -2\omega(\tau_1^{-1} + \tau_2^{-1})$$

In this following Dejean, Lauprêtre, and Monnerie[15–17] case, five parameters were used to fit the data, E_a, activation energy, τ_∞ related to τ_1, and the ratios τ_1/τ_0, τ_2/τ_1. The fitting gave the following values:

$\tau_1 = \tau_\infty \exp(E_a/RT)$
$E_a = 35.3$ kJ/mole
$\tau_\infty = 1.2 \times 10^{-14}$ s
$\tau_1/\tau_0 = 300$
$\tau_2/\tau_1 = 3.1$
$a = 0.42$

In this model the activation energy also lies between 29 and 36 kJ/mole and the uncertainty for the prefactor correlation time is a factor of 5. For "a" the uncertainty is 0.1.

Again, a WLF temperature dependence can be applied to the correlation time τ_1 again yielding a suitable description. The parameters obtained are the following:

$c_1^0 = 5$
$\tau_1(298\ \mathrm{K}) = 2.4 \times 10^{-8}$ s
$\tau_1/\tau_0 = 250$
$\tau_2/\tau_1 = 2.9$
$a = 0.42$

The uncertainties for the correlation times are as before and the uncertainty in c_1^0 is ca. 0.3.

The last spectral density function to be employed corresponds to the Kohlrausch-Williams-Watts (KWW) time correlation function[19–26]

$$\Phi(t) = \exp[-(t/\tau_p)^\alpha]$$

combined with anisotropic restricted rotational diffusion.[11–13] In practice, the stretched exponential is written as a sum exponentials.[25] The composite autocorrelation function including libration that will be integrated to find the spectral density function, has the form[22,23]

$$\Phi(t) = \exp(-t/\tau_0)\Phi_L(t)$$

where $\Phi_L(t)$ is given by[12,13]

$$\Phi_L(t) = A + \frac{B}{2}\{\tfrac{1}{2}A_0^2(\sin\phi) + \tfrac{1}{2}A_0^2(\cos\phi)$$

$$+ \sum_{n=1}^{\infty}[A_n^2(\sin\phi) + A_n^2(\cos\phi)]e^{-\lambda_n t}\}$$

$$+ \frac{C}{2}\{\tfrac{1}{2}A_0^2(\sin 2\phi) + A_0^2(\cos 2\phi)$$

$$+ \sum_{n=1}^{\infty}[A_n^2(\sin 2\phi) + A_n^2(\cos 2\phi)]e^{-\lambda_n t}\}$$

where the A, B, C coefficients have been defined in eq. (1). Angle Δ has also been defined earlier and is equal to 71° and[12,13]

$$A_n(f(\phi)) = \frac{2}{l}\int_0^l f(\phi)\sin\left(\frac{n\pi\phi}{l}\right)d\phi \quad 0 \le \phi \le l$$

The resulting spectral density function is:

$$J(\omega) = \left\{2A + \frac{2B}{l^2}[(1-\cos l)^2 + \sin^2 l]\right.$$

$$\left.+ \frac{C}{2l^2}[(1-\cos 2l)^2 + \sin^2 2l]\right\}J^0(\omega) + B$$

$$\times \sum_{n=1}^{\infty}\left[\left(\frac{1-\cos(l-n\pi)}{l-n\pi} + \frac{1-\cos(l+n\pi)}{l+n\pi}\right)^2\right.$$

$$\left.+ \left(\frac{\sin(l-n\pi)}{l-n\pi} + \frac{\sin(l+n\pi)}{l+n\pi}\right)^2\right]J^{\lambda_n}(\omega) + C$$

$$\times \sum_{n=1}^{\infty}\left[\left(\frac{1-\cos(2l-n\pi)}{2l-n\pi} + \frac{1-\cos(2l+n\pi)}{2l+n\pi}\right)^2\right.$$

$$\left.+ \left(\frac{\sin(2l-n\pi)}{2l-n\pi} + \frac{\sin(2l+n\pi)}{2l+n\pi}\right)^2\right]J^{\lambda_n}(\omega)$$

where

$$J^0(\omega) = \frac{\tau_0}{1+\omega^2\tau_0^2} \quad J^{\lambda_n}(\omega) = \frac{\lambda_n + \tau_0^{-1}}{(\lambda_n + \tau_0^{-1})^2 + \omega^2}$$

$$\lambda_n = \left(\frac{n\pi}{l}\right)^2 D_{ir}$$

In this case six parameters were adjusted; the activation energy associated with τ_0, τ_∞, the angular amplitude l over which rotational diffusion occurs, the rotational diffusion (two parameters), and α, the fractional exponent. The values that were found are:

$\tau_\infty = 1.4 \times 10^{-14}$ s
$E_a = 34.7$ kJ/mole
$\alpha = 0.98$
$l = 5.18T^{0.5}$ (deg)
$D_{ir} = 1.7 \times 10^7 T - 6.5 \times 10^8$ (s^{-1})

It must be noted that τ_p is the characteristic correlation time and sets the position of the distribution associated with the stretched exponential on the time axis. The parameter α, which is between $0 < \alpha < 1$, determines the width of the distribution. The fitting was done by determining first the central

Table I. Proton Line Shape Parameters

Temperature (K)	Gaussian Width (kHz)	Lorentzian Width (kHz)	Fraction Gaussian	Fraction Lorentzian
200	49.0	20.0	0.90	0.10
210	48.0	20.0	0.86	0.14
220	48.0	20.0	0.75	0.25
230	44.0	20.0	0.65	0.35
240	37.0	18.0	0.50	0.50
250	25.0	15.0	0.40	0.60
260	20.0	11.0	0.30	0.70
270	12.0	8.0	0.25	0.75
299	4.0	3.3	0.10	0.90

value of τ_p, for the distribution. Next a series of τ_0 values on both sides of the central value was calculated. A total of 81 τ_0's were used for this fitting. Then for every τ_0, a relaxation time T_1 is calculated and in order to acquire the total relaxation time the individual rates are weighted.[26]

The uncertainty for τ_∞, is again a factor of five and the activation energy lies between 29 and 36 kJ/mole; the uncertainty for α is 0.05, for l is approximately 10° and for D_{ir} about $30 \times 10^8\ \mathrm{s}^{-1}$.

A WLF temperature dependence can again be applied to the correlation time τ_p and the associated fitting parameters are:

τ_p (298 K) = 2.1×10^{-8} s
$c_1^0 = 5$
$\alpha = 0.982$
$l = 5T^{0.5}$ (deg)
$D_{ir} = 1.7 \times 10^7 T$ (s^{-1})

Once more the parameters have not changed very much from those obtained before and the quality of the fitting is approximately the same. The uncertainties are the same as before for all the parameters.

The last spectral density function (Williams-Watts combined with anisotropic rotational diffusion) was also used for fitting the T_1 data for PIB in the PIB–CO_2 system. In this case, all the parameters were kept the same as before, and α was the only parameter that was floated. The value for which the best fit was obtained, is

$$\alpha = 0.91$$

In this case one parameter was used to fit eight experimental data points. As an alternative approach, the activation energy was floated while α was kept constant at 0.98 as in neat PIB. The optimum fitting yielded

$$E_a = 34.3 \text{ kJ/mole}$$

which is approximately the same (within the uncertainty) of the previous fitting, for the neat PIB.

For all the fittings a nonlinear least-squares fitting program was employed to treat the data. The resulting fits have root mean square residuals around 10% or less, which is also the approximate value for the experimental error.

Finally the proton line shapes of pure PIB, shown in Figure 3, were fitted using three parameters. The line shapes were described as a combination of a broad Gaussian component and a narrow Lorentzian component. Three parameters are involved: the width of the Gaussian component, the width of the Lorentzian component, and the fractional population of the Gaussian component. The values obtained are shown in Table I.

For relating polymer dynamics to line shapes, Rössler's formalism[27] of dividing molecular motion into two categories, fast and slow, has gained considerable popularity. Rössler employed a log-Gauss distribution of correlation times which corresponds to a Gaussian function for the energy distribution $g(E)$. There is, however, a technical problem with Rössler's use of the log-Gaussian probability density $g(E)$ in the case of random variables which are nonnegative. The log Gaussian is defined for real variables which are positive or negative. Activation energies are positive only, and the Gaussian corresponds to an unphysical model in this case. A simple alternative distribution is the gamma density, defined for positive random variables only, and the modifications to Rössler's method are sketched briefly below.

We introduce a gamma density distribution of energy barriers

$$\rho(E) = \frac{q(qE)^{\alpha-1}e^{-qE}}{\Gamma(\alpha)}$$

where α and q are two adjustable parameters and $\Gamma(\alpha)$ is a gamma function of α. It follows, then, that the population with activation energy less than E^* is given by:

$$P_{\text{fast}}(E^*) = \int_0^{E^*} \rho(E)\, dE = \frac{q}{\Gamma(\alpha)} \int_0^{E^*} (qE)^{\alpha-1} e^{-qE}\, dE \quad (2a)$$

If we use Rössler's relation, $E^* = RT \ln(\tau^*/\tau_0)$, then we can write equation (a) as:

$$P_{\text{fast}}(T) = \Pi[\alpha, qRT \ln(\tau^*/\tau_0)] \quad (2b)$$

where Π in eq. (2b) is the incomplete gamma function, $1/\tau_0$ is the attempt frequency, and τ^* is the characteristic correlation time determined by the width of the line. The mean activation energy is given by:

$$\langle E^* \rangle = \alpha/q$$

The fitting of the population of the Lorentzian or fast component of the proton line shapes as a function of temperature is shown in Figure 4. The parameters obtained are $\alpha = 50$ and $q = 6.4 \times 10^{-3}$ cal^{-1} with a mean activation energy of $\langle E^* \rangle = 32.7$ kJ/mole. The above values were obtained when $\tau^* = 10^{-5}$ s and $\tau_0 = 10^{-12}$ s as suggested by Rössler. The choice of these characteristic correlation times is somewhat arbitrary and varying them over reasonable ranges changes the estimate of the average energy from 26 to 44 kJ/mole.

DISCUSSION

Any of the three correlation functions or equivalently the three spectral densities provide a suitable basis for the interpretation of the T_1 and NOE data taken on PIB as a function of temperature and Larmor frequency. All of the interpretational functions also produce comparable estimates of the time scale, activation energy, and the effective breadth of the distribution of exponential correlation times. Thus the view of segmental motion developed for PIB is not particularly sensitive to the interpretational model. The Rössler formulation which is also based on the existence of a distribution of correlation times enables one to treat the ^{1}H line shape data, where a correlation function approach is not easily available, and thus make a comparison with the ^{13}C analyses. In this case, reasonable agreement with the activation energies is obtained.

In agreement with the results of Dejean, Lauprêtre, and Monnerie,[7,15-17,28] librational motion must be included to interpret the T_1 data. The Gronski description[12,13] of librational motion when combined with either the Hall-Helfand model[10] or the Kohlrausch-Williams-Watts (KWW) model[19,20] produces a fit of the data which is comparable to the Dejean-Lauprêtre-Monnerie approach. The Gronski model assumes rotation about a single axis and leads to fairly large amplitudes for the librational motion. As can be seen from Figure 5, the amplitude increases from 91° at 313 K to 102° at 383 K. The cone angle in the DLM model is smaller and possibly more realistic. The DLM model treats libration as an activated process while the Gronski approach is just motion in the bottom of a square well. With respect to this latter point, the view of librational motion as an activated process is not so realistic.

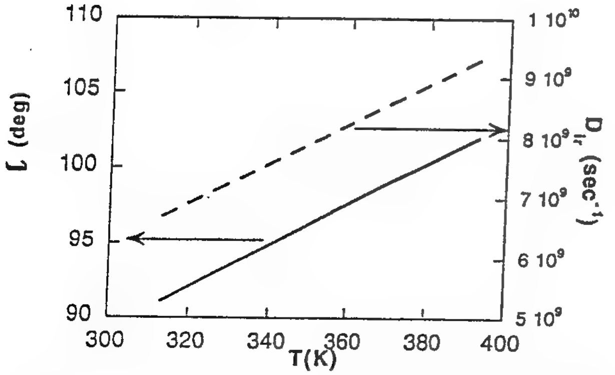

Figure 5. *l* and D_{ir} as a function of temperature; values from the Hall-Helfand model.

The distribution of exponential correlation times is very narrow whichever model is considered though this is most apparent in the context of the KWW model where the exponent approaches unity and thus the distribution collapses to a single exponential. The narrow distribution is in agreement with the strong liquid description of Angell et al.[2] noted in the introduction and the NMR data presented here is one of the better pieces of information available in the literature on the distribution of correlation times in rubbery PIB.

In relation to the original purpose of this study, segmental motion in PIB has a time scale, width of distribution, and activation energy which are close to those observed for the translational diffusion of CO_2 sorbed in PIB. Table II shows a direct comparison of the correlation times for segmental motion of PIB and the correlation times for translational diffusion of CO_2 sorbed in PIB at the same temperatures. The coincidence of the time scales of these two types of motion does not always occur for gases in rubbery polymers since in the only other system[26] [CO_2 sorbed in poly(dimethyl siloxane)] where both motions were studied by NMR, segmental motion is orders of magnitude faster than translational diffusion.[26] It is tempting to cite the low specific volume in PIB as the source of the connection between the time scale of translational diffusion of a penetrant and segmental motion in PIB. In other polymers where less efficient packing is present, a translation jump of a penetrant could occur between two local regions of high free volume uncorrelated to any conformational event in the polymer backbone. In the well-packed PIB, the penetrant might move only when the chain backbone moves. This picture can only be verified through the measurement of the two types of motion in a series of polymer/penetrant systems. It is clear, however, that PIB behaves quite differently from other rubbery polymers both in terms of penetrant diffusion as well as other behaviors.

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NMR STUDY OF SEGMENTAL MOTION IN POLYISOBUTYLENE AND THE RELATIONSHIP TO TRANSLATIONAL DIFFUSION OF SORBED CO_2.

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Introduction

In a previous NMR study(1), the time scale of translational diffusion of CO_2 in PIB on a local level was observed to be close to the time scale of the segmental motion of the polymer. The objective of this report is to more carefully characterize the time scales of segmental motion in PIB using NMR spectroscopy so that link to time scale of penetrant diffusion may be clarified. The Williams - Watts or stretched exponential was used to characterize the distribution of translational correlation times for the CO_2 and it was found to be quite narrow. Comparable information on the segmental motion of the polymer itself appeared not to be readily available lending additional motivation for this study. Based on the strong liquid characterization, a narrow distribution of segmental correlation times would however be expected(2).

Experimental

The PIB sample used for this study was obtained from Cellomer Associates, Inc. of Webster, NY in the form of thick sheets of high molecular weight (Cat. #40E, Lot #02, mol. wt. 1,000,000). NMR experiments were carried out on Bruker SXP (20 - 100), AC - 200 and MSL - 300 spectrometers, which correspond to 22.6 MHz, 50.3 MHz and 75.5 MHz ^{13}C Larmor frequencies respectively. The measurements on the PIB - CO_2 system were made on the AC - 200.

Results

Values of T_1 for the methylene carbon in neat PIB and PIB - CO_2 system, at various temperatures and Larmor frequencies are given in Table I. The NOE as a function of temperature and Larmor frequency is shown in figure 1.

Interpretation

The equations relating the spin - lattice relaxation time and the spectral densities $J(\omega)$ for carbon - 13 nucleus are:

$$\frac{1}{T_1} = W_o + 2\,W_{1C} + W_2$$

$$W_o = \sum_j \gamma_C^2 \gamma_H^2 \left(\frac{h}{2\pi}\right)^2 \frac{J_o(\omega_o)}{20\, r_j^6}$$

$$W_{1C} = \sum_j 3\, \gamma_C^2 \gamma_H^2 \left(\frac{h}{2\pi}\right)^2 \frac{J_1(\omega_C)}{40\, r_j^6}$$

$$W_H = \sum_j 3\, \gamma_H^2 \gamma_C^2 \left(\frac{h}{2\pi}\right)^2 \frac{J_2(\omega_2)}{10\, r_j^6}$$

The equation for the NOE is given by:

$$NOE = 1 + \frac{\gamma_H}{\gamma_C} \frac{6\, J_2(\omega_2) - J_o(\omega_o)}{J_o(\omega_o) + 3\, J_1(\omega_C) + 6\, J_2(\omega_2)}$$

where $\omega_o = \omega_H - \omega_C$ and $\omega_o = \omega_H + \omega_C$. The methylene C - H distance is known from previous studies to be 1.09 Å.

A number of expressions for the spectral density function or alternatively the correlation function have been developed for segmental motion of the polymer. Three correlation functions are used in this study to treat the relaxation data and describe the local motion of the PIB backbone. The first is the Hall - Helfand function combined with anisotropic libration, the second is the Dejean - Lauprêtre - Monnerie function and the third is the Williams - Watts function combined with libration:

$$\Phi(t) = \exp[-(t / \tau_p)^\alpha$$

In practice, the stretched exponential is written as a sum exponentials. The composite autocorrelation function including libration that will be integrated to find the spectral density function, has the form

$$\Phi(t) = \exp(-t / \tau_o)\, \Phi_L(t)$$

where $\Phi_L(t)$ is given by

$$\Phi_L(t) = A + \frac{B}{2}\{ \frac{1}{2} A_0^2(\sin\phi) + \frac{1}{2} A_0^2(\cos\phi) + \sum_{n=1}^{\infty} [A_n^2(\sin\phi) + A_n^2(\cos\phi)]\, e^{-\lambda_n t} \} +$$

$$+ \frac{C}{2}\{ \frac{1}{2} A_0^2(\sin 2\phi) + A_0^2(\cos 2\phi) + \sum_{n=1}^{\infty} [A_n^2(\sin 2\phi) + A_n^2(\cos 2\phi)]\, e^{-\lambda_n t})$$

$$A_n(\,f(\phi)\,) = \frac{2}{\ell} \int_0^{\ell} f(\phi) \sin\left(\frac{n\pi\phi}{\ell}\right) d\phi \qquad\qquad 0 \le \phi \le \ell$$

The resulting spectral density function is:

$$J(\omega) = \{ 2A + \frac{2B}{\ell^2} [(1 - \cos\ell)^2 + \sin^2\ell] + \frac{C}{2\ell^2} [(1 - \cos 2\ell)^2 + \sin^2 2\ell] \}\, J^0(\omega) +$$

$$+ B \sum_{n=1}^{\infty} [(\frac{1 - \cos(\ell - n\pi)}{\ell - n\pi} + \frac{1 - \cos(\ell + n\pi)}{\ell + n\pi})^2 + (\frac{\sin(\ell - n\pi)}{\ell - n\pi} + \frac{\sin(\ell + n\pi)}{\ell + n\pi})^2]\, J^{\lambda_n}(\omega) +$$

$$+ C \sum_{n=1}^{\infty} [(\frac{1 - \cos(2\ell - n\pi)}{2\ell - n\pi} + \frac{1 - \cos(2\ell + n\pi)}{2\ell + n\pi})^2 + (\frac{\sin(2\ell - n\pi)}{2\ell - n\pi} + \frac{\sin(2\ell + n\pi)}{2\ell + n\pi})^2]\, J^{\lambda_n}(\omega)$$

$$J^0(\omega) = \frac{\tau_0}{1 + \omega^2 \tau_0^2} \qquad J^{\lambda_n}(\omega) = \frac{\lambda_n + \tau_0^{-1}}{(\lambda_n + \tau_0^{-1})^2 + \omega^2} \qquad \lambda_n = \left(\frac{n\pi}{\ell}\right)^2 D_{lr}$$

In this case six parameters were adjusted; the activation energy associated with τ_0, τ_∞, the angular amplitude ℓ over which restricted rotational diffusion occurs, the rotational diffusion (two parameters) and α, the fractional exponent. The values are:

$$\tau_\infty = 1.4\ 10^{-14}\ \text{sec}$$

$E_a = 34.7$ kJ / mole

$\alpha = 0.98$

$\zeta = 5.18\ T^{0.5}$

$D_{ir} = 1.7\ 10^7\ T - 6.5\ 10^8$

Discussion

Any of the three correlation functions provide a suitable basis for the interpretation of the T_1 and NOE data taken on PIB as a function of temperature and Larmor frequency. All of the interpretational functions also produce comparable estimates of the time scale, activation energy and the breadth of the distribution of exponential correlation times. Thus the view of segmental motion developed for PIB is not particularly sensitive to the interpretational model.

The distribution of exponential correlation times is very narrow whichever model is considered, though this is most apparent in the context of the Williams - Watts model where the exponent approaches unity and thus the distribution collapses to a single exponential. The narrow distribution is in agreement with the strong liquid description of Angell and the NMR data presented here is one of the better pieces of information available in the literature on the distribution of correlation times in rubbery PIB.

In relation to the original purpose of this study, segmental motion in PIB has a time scale, width of distribution and activation energy which is close to that observed for the translational diffusion of CO_2 sorbed in PIB. Table II shows a direct comparison of the correlation times for segmental motion of PIB and the correlation times for translational diffusion of CO_2 sorbed in PIB at the same temperatures. The coincidence of the time scales of these two types of motion does not always occur for gases in rubbery polymers, since in the only other system (CO_2 sorbed in PDMS) where both motions were studied by NMR, segmental motion is orders of magnitude faster than the translational diffusion(3).

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TABLE I: Methylene carbon T_1 values for neat PIB and for PIB / CO_2 system as a function of temperature at various Larmor frequencies.

T(K)	T_1 (ms) 22 MHz Neat PIB	T_1 (ms) 50.3 MHz Neat PIB	T_1 (msec) 75.4 MHz Neat PIB	T_1 (msec) 50.3 MHz PIB / CO_2
313	44.50	135.66	213.31	103.16
323	41.37	98.79	157.99	86.56
333	41.10	71.06	127.67	79.58
343	42.47	68.04	113.39	73.64
353	53.29	71.04	112.98	74.95
363	64.40	74.48	117.90	79.50
373	62.40	83.20	133.60	83.35
383	81.50	86.85	149.90	-

TABLE II: $(\tau_p)_{DD}$ from reference (1) and τ_p from the Williams - Watts function combined with restricted anisotropic rotational diffusion as a function of temperature.

T(K)	$(\tau_p)_{DD}$ (sec)	τ_p (sec)
313	$1.56\ 10^{-8}$	$8.65\ 10^{-9}$
323	$1.08\ 10^{-8}$	$5.73\ 10^{-9}$
333	$7.64\ 10^{-9}$	$3.88\ 10^{-9}$
343	$5.51\ 10^{-9}$	$2.70\ 10^{-9}$
353	$4.05\ 10^{-9}$	$1.91\ 10^{-9}$
363	$3.02\ 10^{-9}$	$1.38\ 10^{-9}$
373	$2.29\ 10^{-9}$	$1.01\ 10^{-9}$
383	$1.76\ 10^{-9}$	$7.56\ 10^{-10}$

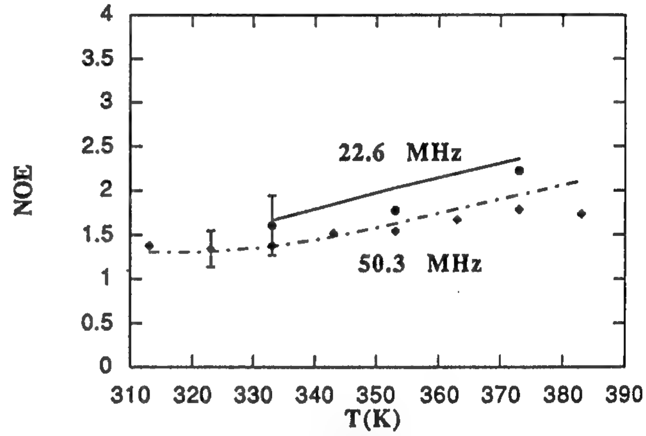

Figure 1. NOE vs Temperature at 22.6 MHz and 50.3 MHz. Lines correspond to the fit for the DLM autocorrelation function. Fits from other models are comparable to the fit shown for the DLM model.

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A Nuclear Magnetic Resonance Study of Dynamics in Toluene - Polyisobutylene Solutions: (I) Penetrant Diffusion and Fujita Theory.

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Abstract

The self - diffusion coefficients of toluene in polyisobutylene (PIB) solutions were determined using the Pulsed Field Gradient Nuclear Magnetic Resonance technique. The volume fraction of toluene in the polymer was varied from 0.045 up to 0.712 and the temperature was varied from 225 K up to 368 K. The concentration dependence of the data was interpreted using the Fujita Free Volume theory and the temperature dependence was interpreted with the WLF equation. These models describe separately the concentration and temperature dependencies of the toluene self - diffusion coefficients very well and the resulting free volume parameters are in a good agreement with the ones extracted from the analysis of viscosity data on the same system.

Keywords: Polyisobutylene, Toluene, Pulse Field Gradient Nuclear Magnetic Resonance, Diffusion, Fujita Free Volume Theory.

Introduction

The diffusion of small molecules into polymers has been the subject of many investigations, because of its importance in industrial, medical and biological applications. Some examples are the membrane separation of gases, controlled drug delivery, control of polymerization, production of barrier materials for the packaging industry and chemical defense. Diffusion of penetrants in polyisobutylene is of special interest since this material displays low permeability for a polymeric rubber well above the glass transition. This unusual property of polyisobutylene has been considered in computer simulations(1) of the rubber and in a detailed characterization of segmental motion(2) in the pure rubber by NMR.

There are a variety of techniques for measuring the self - diffusion coefficients of a penetrant into a polymer matrix. These include sorption, permeation, light scattering, radioactive tracing, forced Rayleigh scattering and Nuclear Magnetic Resonance (NMR). The Pulsed Field Gradient NMR Technique is valuable because it does not perturb the system. With this technique a direct measure of the self - diffusion coefficient of the penetrant is achieved by observing the molecules microscopically, while other methods (sorption method for example) indirectly determine the self - diffusion coefficient from macroscopic measurements. Also the experiment can give information about the geometry of the surroundings of the penetrant molecules in the case of heterogeneous systems; the dimension of the boundaries that the molecules may encounter and the mean square distance that the penetrant has travelled during the observation of diffusion. Other advantages of the technique are the ability to use small sample volumes, the precision of the measurements and the ability to be applied to both liquid and solid samples. The only limitation of the technique is that the lowest diffusion coefficient that can be commonly determined is around 10^{-9} cm^2 / sec to 10^{-10} cm^2 / sec.

In addition to the advantages of Pulsed Gradient technique itself, with NMR the reorientational dynamics of the both the polymeric and penetrant components of the solution can be measured independently on the same sample. Thus both translational and rotational motion of the penetrant, and segmental motion of the polymer can be determined in the same samples. With modern NMR instrumentation, these measurements can be made over a wide range of temperatures and concentrations which lead to a fairly complete description of local dynamics. It is the goal of the series of papers given here to present the results of such a fairly complete set of NMR measurements on a single system beginning with translational diffusion of the penetrant.

Diffusion in polyisobutylene (PIB), has been studied before using different techniques(3 - 7). In references (3) and (4) the study of the diffusion coefficients of six hydrocarbons (propane, n - butane, isobutane, n - pentane, isopentane and neopentane) in PIB was reported using the sorption method. The self - diffusion of benzene in PIB has been studied in reference (5) using the pulsed field gradient technique over a limited range of temperatures and concentrations. In reference (6) the diffusion of radioactively tagged cetane in PIB has been studied and finally in reference (7) the diffusion of toluene in butyl rubber has been studied using the sorption method. In all cases the data were analyzed using the Fujita free volume theory. Viscosity data on polyisobutylene solutions are also available(8 - 11). In references (8 - 10) the intrinsic viscosities of PIB solutions in various solvents have been studied and their relations to polymer chain structure and to thermodynamic parameters governing the interaction between the polymer and the solvent have been made.

Free volume theories have been used widely for the interpretation of the concentration dependence of the self - diffusion of many small molecules into polymer matrices(12 - 15). One frequently used theory, developed almost thirty years ago(12), is the Fujita theory which will be employed in this paper to summarize penetrant motion. In the second report of this series, the same penetrant data will be reanalyzed with a more recent free volume theory, that of Vrentas and Duda. These two free volume theories differ in several respects and it will be of value to compare them in the context of a rather complete data set not only including information of translational motion of the penetrant but also reorientational motion of both components: polymer and penetrant. The molecular level information available from NMR will provide insight into some of the concepts introduced into these theories which are at least at first glance based on very local descriptions of polymer and solvent dynamics.

The Fujita theory begins with the empirical result of Doolittle(16 - 17) who showed that the viscosity η of a liquid of low molecular weight is given by:

$$\ln\eta = \ln A + B / f \qquad (1)$$

where A and B are empirical constants for a given liquid and f is the fractional free volume, defined to be equal to the ratio of the volume of the space not occupied by the constituent molecules, v_f, over the total volume of the solution, v:

$$f = \frac{v_f}{v} \qquad (2)$$

$$v = v_0 + v_f \qquad (3)$$

where v_0 is the volume occupied by the molecules in accordance with Van der Waals radii and vibrational motions. Equation (1) measures the volume of a molecule relative to the volume of a void next to it. When the volume of the void is larger than the volume of the molecule the viscosity is low. When the volume of the void is smaller than the volume of the molecule the viscosity is high. Another assumption that is made is that the Doolittle relation applies to each jumping unit in polymer - solvent systems(18). Jumping units are imagined to be of the size of small penetrant molecules or repeat units in the case of the polymer. Also the theory relates the mobility of the polymer and the solvent jumping units to the free volume per unit volume of solution.

In this study the temperature and concentration dependencies of the self - diffusion of toluene in PIB generated from the Pulsed field gradient technique will be examined and then a comparison with viscosity data from macroscopic techniques will be attempted. The concentration dependence of the data will be analyzed with the Fujita theory(12) while the temperature dependence will be analyzed using the WLF equation for diffusion(19), which is also commonly placed in the context of free volume theories. The well known form of the WLF equation is

$$\log_{10}\frac{\zeta}{\zeta_0}=\frac{-c_1^D(T-T_0)}{c_2^D+T-T_0} \qquad (4)$$

where ζ is the translational friction coefficient of a penetrant molecule into the polymer matrix, ζ_0 is the value of ζ at T_0 and $c_1{}^D$ and $c_2{}^D$ are the WLF coefficients at the reference temperature T_0. The diffusion coefficient ,D ,can be introduced into this equation by using the well known expression :

$$D=\frac{kT}{\zeta} \qquad (5)$$

where k is the Boltzmann's constant. The WLF equation can thus be applied to diffusion.

Experimental

The polyisobutylene sample used for the study was obtained from Cellomer Associates, Inc. of Webster, NY in the form of thick sheets of high molecular weight (Cat. #40E, Lot #02, mol. wt 1,000,000). HPLC Grade toluene was obtained from FisherChemical Fisher Scientific. The diffusion measurements were performed on a Bruker MSL - 300 spectrometer equipped with a High Resolution Diffusion Unit and gradient probe, with a proton frequency of 300.1 MHz. For the diffusion measurements the phenyl proton peak of toluene was observed.

The well known Stejskal - Tanner pulse sequence(20) π / 2 - G(δ) - π - G(δ) - (echo) was used to measure the diffusion coefficient of toluene in PIB solutions. The stimulated echo(21) pulse sequence π / 2 - G(δ) - π / 2 - τ - π / 2 - G(δ) - (echo) was also used for measuring the diffusion coefficient, employing longer diffusion time observations. The strength of the magnetic field gradients was varied from 14 gauss / cm up to 140 gauss / cm; the associated length δ, from 500 µsec up to 7 msec; and the distance between the two gradient pulses Δ, from 2 msec up to 80 msec. Those values of Δ correspond to diffusion distances from approximately 1.1 µm up to 9.1 µm.

Interpretation

The temperature dependence of toluene in PIB was analyzed with the following form of the WLF equation(19):

$$\log_{10}\left(\frac{DT_0}{D_{T_0}T}\right) = \frac{c_1^D(T-T_0)}{c_2^D + T - T_0} \qquad (6)$$

where $c_1{}^D = B_d / 2.303\, f(\phi_S)$, $c_2{}^D = f(\phi_S) / \alpha(\phi_S)$, $f(\phi_S)$ is the fractional free volume of the solution at the reference temperature T_0, ϕ_S is the volume fraction of toluene in PIB and $\alpha(\phi_S)$ is the fractional free volume expansion factor and D_{T_0} is the self diffusion coefficient at T_0. Equation (6) can be rewritten as:

$$\ln\left(\frac{DT_0}{D_{T_0}T}\right) = \frac{\frac{\alpha(\phi_s)}{B_d}(T-T_0)}{\frac{f(\phi_s)}{B_d}\left(\frac{f(\phi_s)}{B_d} + \frac{\alpha(\phi_s)}{B_d}(T-T_0)\right)} \qquad (7)$$

The parameters that were floated in order to fit the data were $\alpha(\phi_S) / B_d$ and $f(\phi_S) / B_d$. B_d is analogous to the B in equation (1) and will be defined precisely later. The fits along with the experimental self - diffusion coefficients at different concentrations and temperatures, are shown in Figure 1, and the reference temperature T_0 was chosen to be 298 K. The parameters obtained are shown in Table 1. After $\alpha(\phi_S)/B_d$ and $f(\phi_S)/B_d$ were obtained, the WLF coefficients $c_1{}^D$ and $c_2{}^D$ were calculated (from $c_1{}^D = B_d / 2.303\, f(\phi_S)$ and $c_2{}^D = f(\phi_S) / \alpha(\phi_S)$) and they are also shown in Table 1.

To fit the data at a constant temperature, as a function of concentration, the Fujita free volume theory(12) was applied. As mentioned above, the theory begins with the result of Doolittle(16 - 18) who showed that the viscosity η of ordinary liquids of low molecular weight is given by equation (1).

To relate this to diffusion, the mobility, m, of a molecule is considered to be the velocity with which a molecule translates under the action of unit force and is inversely proportional to the molecular friction coefficient and the viscosity η (Stokes law). Thus equation (1) can be written as:

$$\ln(m) = C - B / f \qquad (8)$$

where C is a constant. The mobility of a molecule in a medium depends on the probability that the molecule will find in its vicinity a hole which is large enough to allow displacement into it. The constant B is considered to be a measure of the size of a given hole. Let B_d be the value of B for the minimum hole which is needed to allow a given molecule to undergo such a displacement(12),(22). Therefore equation (8) will become:

$$\ln(m) = A - B_d / f \qquad (9)$$

The definition of mobility in terms of the self - diffusion coefficient of a penetrant in a polymer matrix is(23):

$$D = R\,T\,m \tag{10}$$

where R is the gas constant, T is the absolute temperature and D is the self - diffusion coefficient.

In general the free volume of a given polymer - penetrant solution depends on temperature and concentration and it is more appropriate to denote the fractional free volume as $f(T, \phi_s)$ where again ϕ_s is the volume fraction of the penetrant. It has been shown(24) that if the increase in free volume by the addition of the diluent is proportional to the volume of the added penetrant, then:

$$v_f = (v_f)_2 + \gamma(T)\,v_1 \tag{11}$$

$$v = v_1 + v_2 \tag{12}$$

where v_f is the average free volume of the solution, $(v_f)_2$ is the average free volume of the pure polymer, $\gamma(T)$ is a proportionality factor that may be compared with the fractional free volume of the diluent, v is the total volume of the solution, v_1 is the volume of the penetrant and v_2 is the volume of the amorphous polymer. By dividing equation (11) with equation (12) the fractional free volume of the solution $f(T, \phi_s)$ is found to be a linear function of the volume fraction of the penetrant ϕ_s:

$$f(T, \phi_s) = f_p(T, 0) + (\,f_s(T) - f_p(T, 0)\,)\,\phi_s \tag{13}$$

where $f_p(T, 0)$ is the fractional free volume of pure polymer and $f_s(T)$ is a parameter that represents the fractional free volume of the solvent trapped in the polymer matrix. $f_s(T) - f_p(T, 0)$ represents the effectiveness of the penetrant for increasing the free volume when it is dispersed in the given polymer. Equation (13) can be rewritten as:

$$\frac{f(T,\phi_s)}{B_d} = \frac{f_p(T)}{B_d} + \left(\frac{f_s(T)}{B_d} - \frac{f_p(T)}{B_d}\right)\phi_s \tag{14}$$

If equations (13) and (9) are substituted into equation (10) considering that as $\phi_s \to 0$, $D \to D_0$ we obtain:

$$\ln\frac{D}{D_0}=\frac{B_d(f_s-f_p)\phi_s}{f_p^2+(f_s-f_p)f_p\phi_s}=\frac{[(\frac{f_s}{B_d})-(\frac{f_p}{B_d})]\phi_s}{(\frac{f_p}{B_d})^2+[(\frac{f_s}{B_d})-(\frac{f_p}{B_d})](\frac{f_p}{B_d})\phi_s} \qquad (15)$$

where ϕ_S is the penetrant volume fraction, D_0 is the diffusion coefficient of toluene at the limit of zero penetrant concentration, f_p is the average fractional free volume of pure polymer and f_s is the fractional free volume of toluene in the solution.

For each temperature, the diffusion coefficient of toluene as a function of concentration was fitted using equation (15). The parameters varied are D_0, (f_p / B_d) and (f_s / B_d). The reason for using (f_p / B_d) and (f_s / B_d) as fitting parameters and not f_p and f_s is to avoid making any assumptions about the parameter B_d. The parameters (f_p / B_d) and (f_s / B_d) do not have physical significance whereas f_p, f_s and B_d do. The parameters produced by the fit are shown in Table 2 and the lines corresponding to the fit in Figures 2 and 3.

From the diffusion coefficient of toluene at the limit of zero penetrant concentration in Table 2 and the WLF equation (6), WLF parameters can be obtained similar to those shown in Table 1. Those are shown in the Table 3 below.

Discussion

A comparison can be made between the fractional free volume determined from the temperature dependence of the translational diffusion of the toluene with that determined from the concentration dependence of the same quantity. Such a comparison is made in Figure 4 where the fractional free volume of the solution, $f(T, \phi_S)$, is presented as a function of the volume fraction of toluene in PIB. The points come from Table 1 and they were obtained from the WLF equation (7) where the temperature dependence of the toluene self - diffusion was analyzed, except the filled circle that represents the fractional free volume of pure toluene (at 293 K) obtained from viscosity data(25). The solid line was obtained from equation (14) using the values of Table 2 for $f_p(T)$ and $f_s(T)$ (obtained from equation (15) where the concentration dependence of the toluene self - diffusion was analyzed). The error bars represent an uncertainty of approximately 20% for $f(T, \phi_S)$ in Table 1, which comes from quality of the fitting (namely the fitting of the temperature dependence of the self - diffusion of toluene in PIB). As can be seen from Figure 4, the values of the fractional free volume of the solution that are obtained from the analysis of the temperature and concentration dependencies of the self - diffusion of toluene in PIB, are, in fact, close to each other.

The thermal expansion coefficients of the fractional free volume obtained from this work can be compared with typical literature values obtained from viscosity data as is shown in Figure 5. The points come from Table 1 and they were obtained from equation (7) when the temperature dependence of the toluene self - diffusion was analyzed. The solid line was obtained from equation (16):

$$\alpha(\phi_S) = (1 - \phi_S)\,\alpha_p + \phi_S\,\alpha_S \qquad 16)$$

with the literature values(19, 25) of α_p = 4.4 10^{-4} deg^{-1} and α_S = 1.7$10^{-3}$ deg^{-1} (at 293 K), where subscripts p and s refer to polymer and solvent respectively. The error bars represent an uncertainty of approximately 20% for $\alpha(\phi_S)$ in Table 1, which comes from quality of the fitting of the temperature dependence of the self - diffusion of toluene in PIB. Reassuringly, again the two sets of data are in good agreement with each other.

A free volume analysis of the viscosity of the toluene - PIB solution was done by Fujita(25). In that study the fractional free volume of the solution, f(293 K, ϕ_S), and the fractional free volume of toluene trapped in the polymer matrix, f_S(293 K), are reported as a function of concentration at 293 K. In reference (23) the author uses the following equation, for the viscosity data analysis, with the assumption that B_p = 1:

$$\frac{f(293K,\phi_s)}{B_p} = \frac{f_p(293K)}{B_p} + \left(\frac{f_s(293K)}{B_p} - \frac{f_p(293K)}{B_p}\right)\phi_s \qquad (17)$$

where B_p represents the minimum void necessary for one flow unit to be displaced (i.e. the analog of B_d for viscous flow). The values that are derived are(25):

$$f_p\,(293\ K) = 0.048 \qquad f_S(293\ K) - f_p\,(293\ K) = 0.052 \qquad (18)$$

In order to obtain a meaningful comparison with this viscosity data it would be desirable to calculate the quantities f(293K, ϕ_S), f_p(293 K) and f_S(293 K) - f_p(293 K) from the diffusion results . From Table 2 the values of f_S / B_d and f_p / B_d can be extrapolated to 293 K following the form f (T) = f(T_0) + α (T - T_0) yielding :

$$f_S\,(293\ K) / B_d = 0.263 \quad f_p\,(293\ K) / B_d = 0.084 \qquad (19)$$

Using equation (14) for T = 293 K and the values shown in equation (19) the parameter B_d, which is a measure of the minimum void size required for penetrant (toluene) displacement, is varied in order to match the viscosity data. The best match of the free volume curves versus volume fraction toluene is shown in Figure 6. The values derived from this procedure for the minimum necessary void size for diffusion are between 0.4 and 0.45. This is a very approximate estimate for B_d since an extensive viscosity data set as a function of concentration that might be compared with the diffusion data presented here, was not available. For B_d between 0.4 and 0.45 the intercept and slope of the dotted line in Figure 6 for diffusion data corresponding to equation (14) yields :

$$f_p\ (293\ K)\ \text{between}\ 0.0336\ \text{and}\ 0.0378$$

$$f_s\ (293\ K) - f_p\ (293\ K)\ \text{between}\ 0.072\ \text{and}\ 0.081$$

These values are to be compared with those given in equation (18). The differences between the values obtained from the diffusion data and the viscosity data may be attributed to B_p which is assumed to be equal to 1 in the viscosity data analysis, the uncertainties of the free volume parameters, the accuracy of the viscosity and diffusion data and the uncertainties in the knowledge of the α_p and f_g (the fractional free volume of PIB at the glass transition temperature) for PIB.

It would have been better to calculate B_d from the slope of the following equation(12):

$$\ln\left(\frac{D}{D_0}\right) = \frac{B_d}{B_p} \ln\left(\frac{\eta(T,0)(1-\phi_s)}{\eta(T,\phi_s)}\right) \qquad (20)$$

with B_p set equal 1, but extensive viscosity data as a function of toluene concentration were not available. If B_p is not assumed to be equal to 1, then the ratio B_d / B_p is estimated.

From the temperature dependence of f_p / B_d a value for the free volume expansion coefficient α_f can be obtained (given the determination of B_d as between 0.4 and 0.45) utilizing the following equation:

$$f_p(T) = f_p(T_0) + \alpha_f(T - T_0) \qquad (21)$$

The value for α_f is found to be between 3.38×10^{-4} and 3.8×10^{-4} deg^{-1} which is close to the values reported elsewhere from viscosity data(19) which range from 4.4 10^{-4} deg^{-1} to 2.5 10^{-4} deg^{-1}. Figure 7 shows the temperature dependence of f_p for $B_d = 0.4$ and for $B_d = 0.45$.

Figure 8 shows a comparison of the free volume of neat toluene as a function of temperature obtained from viscosity data(25) and the free volume of toluene trapped in PIB obtained from the diffusion data presented here (Table 2). It shows that the fractional free volume of toluene decreases when the latter is trapped in entangled PIB in agreement with the conclusion in reference (25).

In Figure 9 the fractional free volume of the PIB component in the solution (extracted from the diffusion data presented in this study; Table 2) is compared with the free volume parameters obtained from other studies of penetrants in polyisobutylene(5 - 6, 19). In this case the minimum void size B_d was assumed to be 1. The limited fractional free volume data from other diffusion studies(5 - 6) are closer to the values determined in this work than the values determined from viscosity(19) .

Finally, looking at the enthalpy of activation for diffusion, an Arrhenius temperature dependence was given to the self - diffusion coefficient of toluene:

$$D = D_1 \exp(-\Delta H_D / RT) \qquad (22)$$

Plotting lnD as a function of 1 / T(K) the enthalpy activation energy for diffusion is calculated. In this procedure the non-linearity which can be seen in Figure 1 and is reflective of non-Arrhenius behavior is ignored. The values obtained, for different concentrations, are shown in Table 4. The value, 13.5 kJ / mole, for pure toluene is close to the value (10.9 kJ / mole) reported elsewhere(26).

When lnD is not a linear function of (1 / T), a temperature dependent "apparent" activation energy can be calculated from the WLF equation, in terms of the shift factor a_T, formally as(6, 19):

$$E_D = R\frac{d(\ln a_T)}{d(\frac{1}{T})} \qquad (23)$$

If $\ln a_T$ is given by a WLF equation(19), then a temperature dependent apparent activation energy controlled by free volume considerations can be obtained(6, 19):

$$E_D = \frac{2.303 R c_1^D c_2^D T^2}{(c_2^D + T - T_0)^2} \qquad (24)$$

Since the WLF coefficients are available from the information in Table 1 and for $T = T_0 = 298$ K, $c_1{}^D = B_d / 2.303 f(\phi_s)$, $c_2{}^D = f(\phi_s) / \alpha(\phi_s)$ equation (24 becomes:

$$E_D = \frac{R(298)^2(\frac{\alpha_f}{B_d})}{(\frac{f(\phi_s)}{B_d})^2} \qquad (25)$$

Thus from equation (25) and Table 1, we obtain Table 5. A comparison of the activation energies shown in Tables 4 and 5 is shown in Figure 10.

Finally using equation (23) with $T_0 = 298$ K and the WLF coefficients $c_1{}^D$, $c_2{}^D$, taken from Table 1, the activation energy of each concentration as a function of temperature is calculated. The results are shown in Figure 11. Essentially, the activation energies determined from either approach are within experimental error of each other though those obtained from equation (25) more accurately reflect the trends, particularly at higher polymer contents. It is clear from Figure 11 that the temperature dependence of the activation energy increases with polymer content and the apparent activation energy increases rapidly with decreasing temperature as expected from WLF predictions. In contrast the behavior at high solvent content is essentially temperature independent and more characteristically Arrhenius as expected.

Conclusions

It is clear from the above analysis that the concentration dependence of the self - diffusion coefficient of toluene in PIB is well described by the Fujita fractional free volume theory. Also it is clear that the temperature dependence of the self - diffusion coefficient of toluene in PIB is well described by the WLF equation for diffusion. In addition it has been established that the fractional free volumes and the fractional free volume thermal expansion coefficients of the solutions calculated from the temperature dependence of the self - diffusion coefficient of toluene in PIB (equation (6)) are close to the values obtained from the analysis of the concentration dependence of the self - diffusion coefficient of toluene in PIB (equation (7)); a fact that lends credibility to the validity of the interpretation.

Also the fractional free volumes of the solutions at 293 K obtained from the self - diffusion data are close to the values obtained from the viscosity data. This establishes the utility of the free volume approach in relation to molecular mobility of a penetrant in a polymer. Viscosity is macroscopic measure, while the diffusion measurements presented here are microscopic measurements looking specifically at the penetrant molecule. Two different experiments probing two different levels of dynamics give approximately the same fractional free volume for the solutions, when the appropriate value for the minimum void size necessary for diffusion relative to viscosity was chosen.

Another result that has been confirmed, is the decrease of the fractional free volume of toluene when the latter is trapped in entangled PIB. The same conclusion has been reached from viscosity data(25), with a completely different approach. Also the fractional free volume parameters for pure PIB obtained from this work are close to the values reported in the literature and extracted from other diffusion or viscoelastic measurements. This confirms the correctness of the magnitude of the free volume of the particular polymer.

From the preceding analysis it is obvious that B_d, the parameter that represents the minimum void size necessary for a penetrant molecule to diffuse, is important if results obtained from different methods that observe different kind of motions are to be compared. This is to be expected since the size of a moving unit is not the same for different kind of motions. The unfortunate fact is that it is not possible to obtain the dimension of the void when the parameter B_d is known.

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Table 1

Parameters obtained from the temperature dependence fit of the toluene self - diffusion coefficient, using equation (6).

ϕ_s	$f(\phi_s) / B_d$	$\alpha(\phi_s) / B_d$ (deg^{-1})	c_1^D	c_2^D (K)
0.045	0.0904	$5.83\ 10^{-4}$	4.803	155.060
0.104	0.1050	$6.84\ 10^{-4}$	4.135	153.509
0.205	0.1270	$7.25\ 10^{-4}$	3.419	175.172
0.327	0.1550	$8.44\ 10^{-4}$	2.801	183.649
0.409	0.1900	$9.60\ 10^{-4}$	2.285	197.917
0.712	0.2700	$1.10\ 10^{-3}$	1.608	245.455
1.000	0.3700	$1.70\ 10^{-3}$	1.174	217.647

Table 2

Parameters obtained from the concentration dependence fit of the toluene self - diffusion coefficient, using equation (15).

T(K)	f_s / B_d	f_p / B_d	D_0 (cm^2 / sec)
298	0.273	0.08735	$9.08\ 10^{-9}$
310	0.300	0.09780	$2.55\ 10^{-8}$
320	0.333	0.10700	$5.15\ 10^{-8}$
329	0.364	0.11630	$8.70\ 10^{-8}$
339	0.381	0.12500	$1.55\ 10^{-7}$
349	0.398	0.13200	$2.30\ 10^{-7}$
358	0.423	0.14100	$3.40\ 10^{-7}$
368	0.449	0.14450	$4.10\ 10^{-7}$

Table 3

Parameters obtained from the temperature dependence fit of the toluene self - diffusion coefficient at zero toluene concentration (D_0, shown in Table 2), using equation (6).

ϕ_s	$f(\phi_s) / B_d$	$\alpha(\phi_s) / B_d$ (deg^{-1})	c_1^D	c_2^D (K)
0.000	0.0818	$5.34\ 10^{-4}$	5.308	153.184

Table 4

Apparent activation energy for diffusion of toluene in PIB as a function of concentration, obtained from the lnD vs 1 / T plot of the self - diffusion coefficient of toluene in PIB (Arrhenius temperature dependence).

ϕ_s	ΔH_D (kJ / mole)
0.000	50.4
0.045	44.4
0.104	40.4
0.205	34.1
0.327	28.6
0.409	22.5
0.712	12.4
1.000	13.5

Table 5

Apparent activation energy for diffusion of toluene in PIB, controlled by free volume, as a function of concentration, obtained from equation (25) and Table 1.

ϕ_s	E_D (kJ / mole)
0.000	58.9
0.045	52.6
0.104	45.8
0.205	33.1
0.327	25.9
0.409	19.6
0.712	11.1
1.000	9.16

Figure Captions

Figure 1: Self - diffusion coefficient of toluene in PIB solutions as a function of temperature at different concentrations. The solid lines represent fits to the WLF diffusion equation presented in the text. The zero penetrant (0%) concentration points are from Table 2.

Figure 2: Self - diffusion coefficient of toluene in PIB solutions as a function of concentration at different temperatures. Solid lines represent fits to Fujita free volume theory presented in the text.

Figure 3: Self - diffusion coefficient of toluene in PIB solutions as a function of concentration at different temperatures. Solid lines represent fits to Fujita free volume theory presented in the text.

Figure 4: Comparison of the fractional free volume of the toluene - PIB solution, obtained from the temperature (points) and concentration (line) dependence of the diffusion coefficient. Solid line represents values obtained from equation (14). Filled circle represents the fractional free volume of pure toluene at 293 K(25).

Figure 5: Thermal expansion coefficient of the solution fractional free volume as a function of the volume fraction of toluene in polyisobutylene. Points represent values from Table 1 and the solid line represents values obtained from equation (16) with $\alpha_p = 4.4\ 10^{-4}$ deg^{-1} and $\alpha_s = 1.7\ 10^{-3}\ \mathrm{deg}^{-1}$.

Figure 6: Comparison of fractional free volume of the toluene - PIB solution as a function of concentration obtained from diffusion data for $B_d = 0.45$ (dashed line) with the values obtained from viscosity data (solid line) from reference (25), for $B_p = 1$. The dashed line was calculated from equation (14) for $T = 293$ K.

Figure 7: Fractional Free Volume of the polyisobutylene component in the solution as a function of Temperature using different values for B_d; Solid lines represent curve fitting according to equation (21).

Figure 8: Comparison of the fractional free volume of neat toluene(12) with the fractional free volume of toluene trapped in PIB, as a function of temperature.

Figure 9: Comparison of the fractional free volume of the polyisobutylene component in the solution with reported values in the literature as a function of temperature.

Figure 10: Activation energy for diffusion as a function of the volume fraction of toluene in PIB. Open circles represent values obtained from an Arrhenius temperature dependence of the self - diffusion coefficient of toluene in PIB. Filled circles were calculated from equation (25).

Figure 11: Apparent activation energy for diffusion, controlled by free volume, as a function of temperature for each concentration, obtained from equation (23).

fig 1

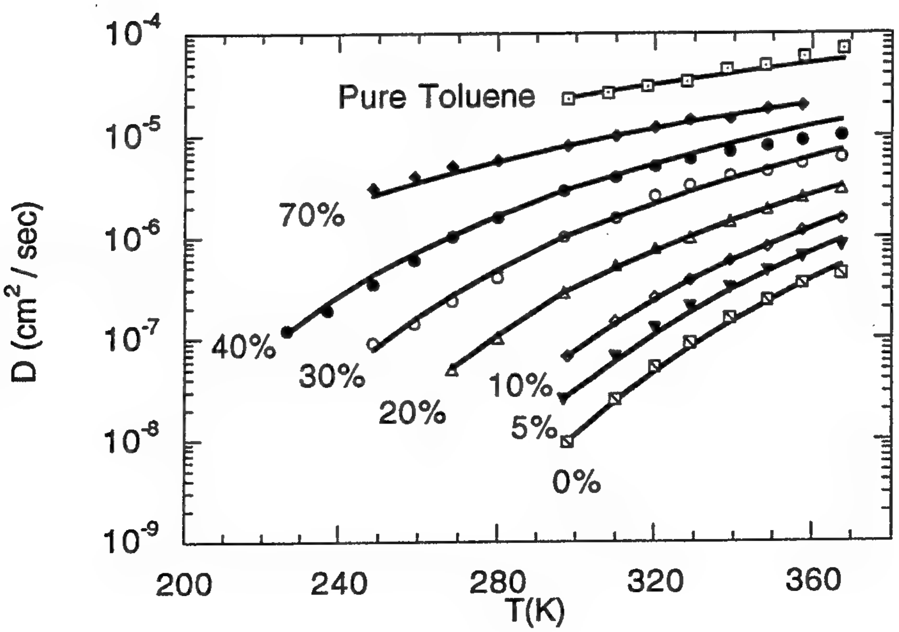


fig 2

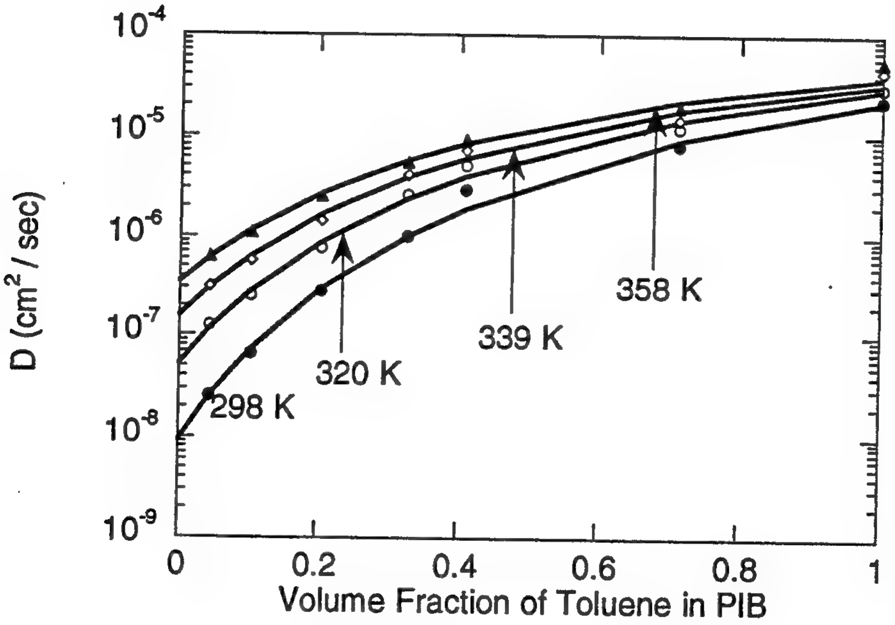

10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
D (cm^2 / sec)
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene in PIB
298 K
320 K
339 K
358 K

fig 3

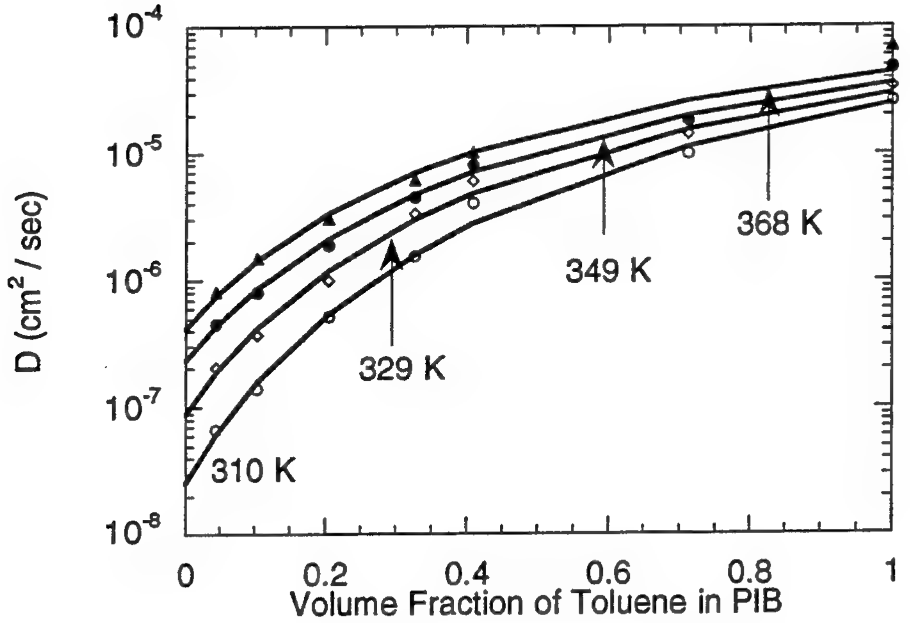

10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
D (cm^2 / sec)
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene in PIB
368 K
349 K
329 K
310 K

fig 4

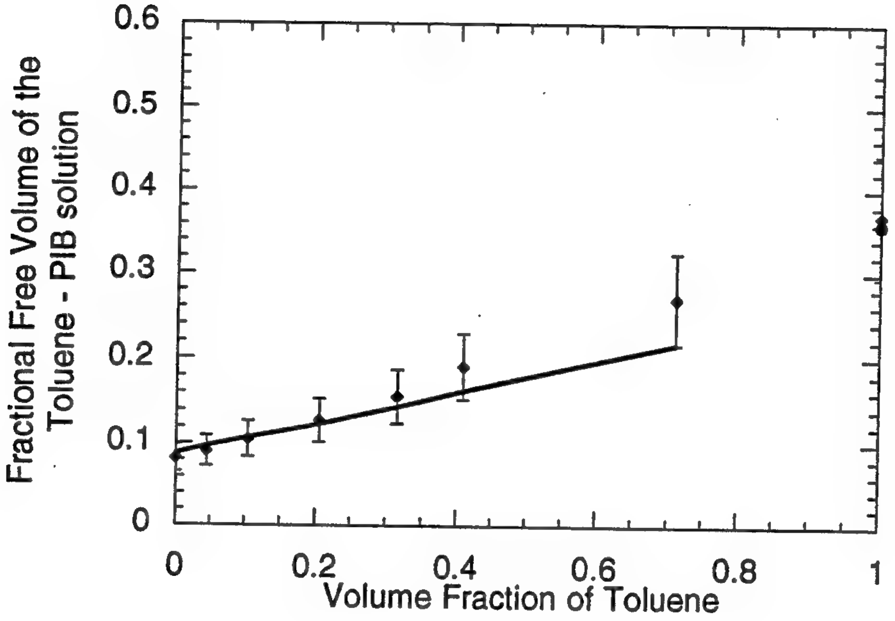

0.6
0.5
0.4
0.3
0.2
0.1
0
Fractional Free Volume of the Toluene - PIB solution
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene

fig 5

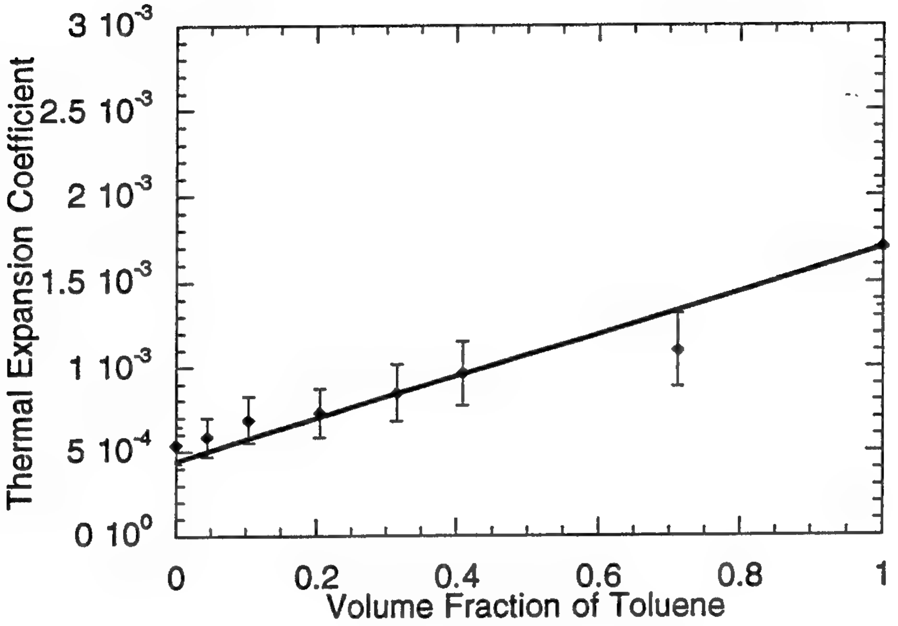
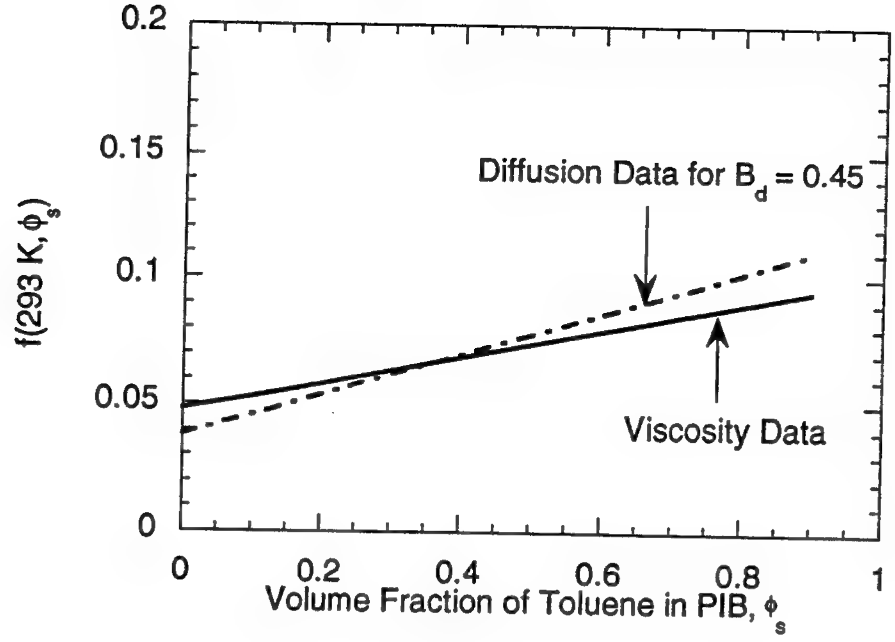

3 10^{-3}
2.5 10^{-3}
2 10^{-3}
1.5 10^{-3}
1 10^{-3}
5 10^{-4}
0 10^{0}
Thermal Expansion Coefficient
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene

fig 6


0.2
0.15
0.1
0.05
0
f(293 K, ϕ_s)
Diffusion Data for B_d = 0.45
Viscosity Data
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene in PIB, ϕ_s

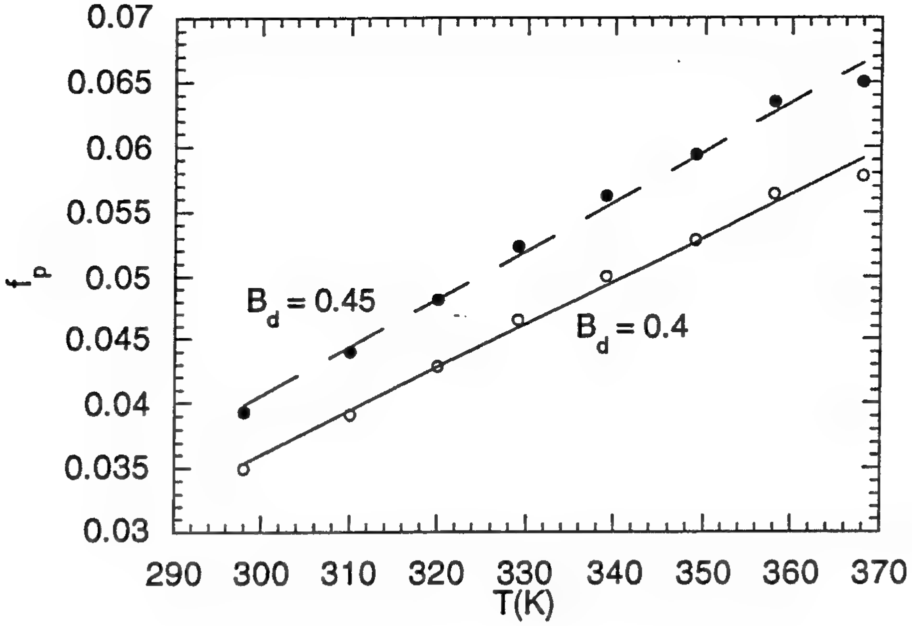

0.07
0.065
0.06
0.055
0.05
0.045
0.04
0.035
0.03
f_p
$B_d = 0.45$
$B_d = 0.4$
290
300
310
320
330
340
350
360
370
T(K)

fig 7

fig 8

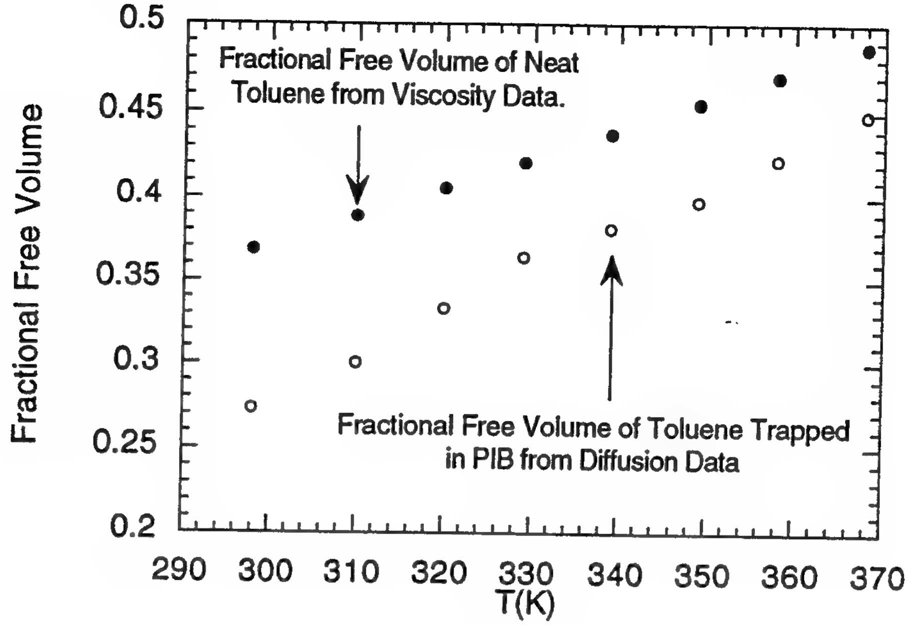

Fractional Free Volume
0.5
0.45
0.4
0.35
0.3
0.25
0.2
290
300
310
320
330
340
350
360
370
T(K)
Fractional Free Volume of Neat Toluene from Viscosity Data.
Fractional Free Volume of Toluene Trapped in PIB from Diffusion Data

fig 9

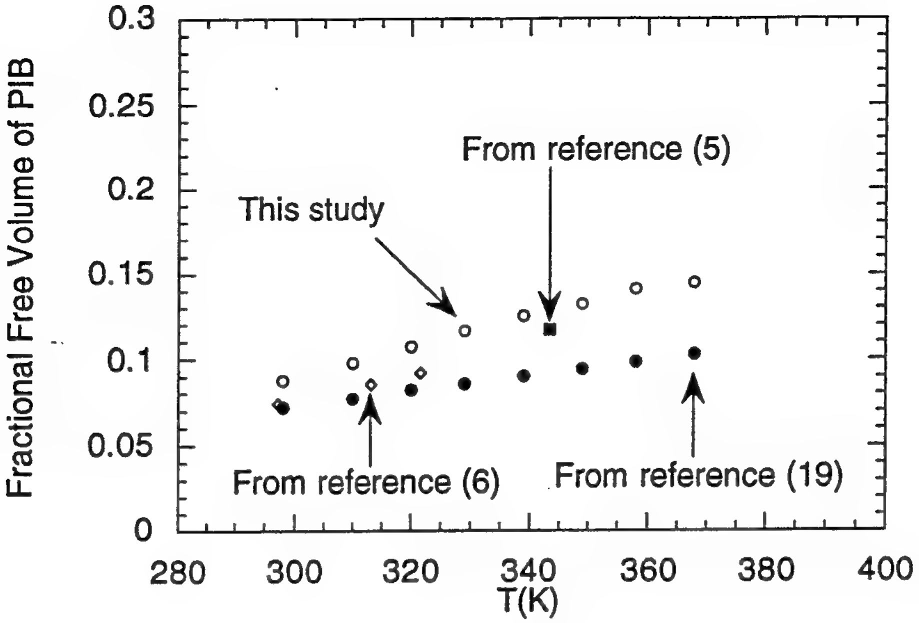

Fractional Free Volume of PIB
0.3
0.25
0.2
0.15
0.1
0.05
0
280
300
320
340
360
380
400
T(K)
This study
From reference (5)
From reference (6)
From reference (19)

fig 10

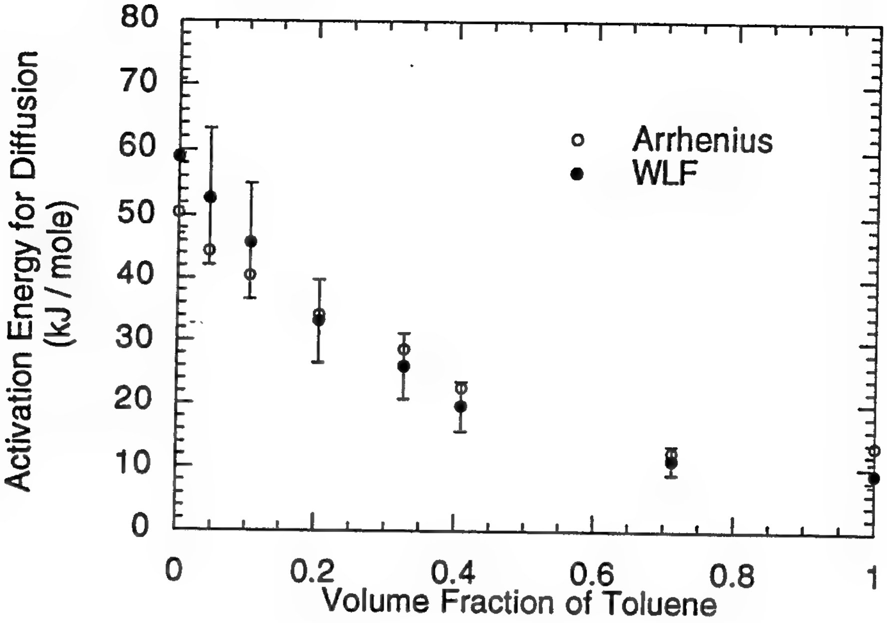
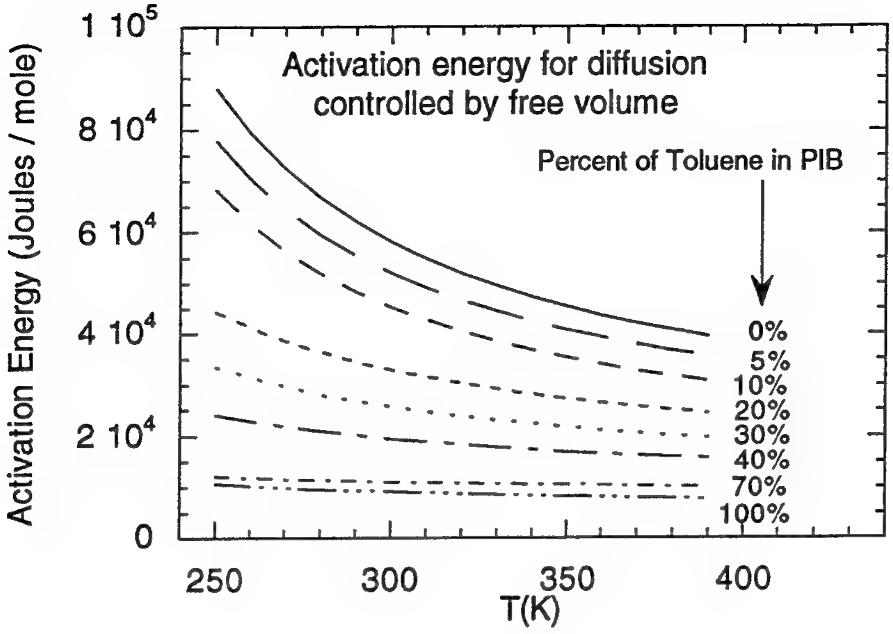

Activation Energy for Diffusion
(kJ / mole)
80
70
60
50
40
30
20
10
0
Volume Fraction of Toluene
0
0.2
0.4
0.6
0.8
1
○ Arrhenius
● WLF

fig 11


Activation energy for diffusion controlled by free volume
Percent of Toluene in PIB
0%
5%
10%
20%
30%
40%
70%
100%
Activation Energy (Joules / mole)
1 10^5
8 10^4
6 10^4
4 10^4
2 10^4
0
250
300
350
400
T(K)

A Nuclear Magnetic Resonance Study of Toluene - Polyisobutylene Solutions. (II) Vrentas - Duda Theory.

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Abstract

The self - diffusion coefficients of toluene in polyisobutylene have been analyzed using the Vrentas - Duda free volume diffusion model. The diffusion coefficients were determined at different temperatures and concentrations, using the pulsed field gradient nuclear magnetic resonance technique. The data were satisfactorily described by the model and the size of the polymer jumping unit was extracted. Comparisons were made with the Fujita free volume theory and the Fujita free volume parameters were extracted from the Vrentas - Duda free volume parameters. From the diffusion data that now available, it can be concluded that for most polymers the jumping unit is about 1.5 times the polymer monomer molecular weight. The activation energy of the toluene diffusion in polyisobutylene is compared with the activation energies of other penetrants in the same polymer. The diffusion data presented in this work show that the energy per mole required to overcome the attractive forces which constrain a diffusing species to its neighbors should be considered to be zero, in order to be able to extract the free volume parameters (from viscosity and diffusion data) with an acceptable uncertainty.

Keywords: Polyisobutylene, Toluene, Pulsed Field Gradient Nuclear Magnetic Resonance, Diffusion, Vrentas - Duda Theory, Fujita Theory.

Introduction

In the previous paper(1), the self - diffusion coefficients of toluene in polyisobutylene (PIB), as measured by the pulsed field gradient NMR technique, have been presented as a function of temperature and concentration and analysed using the Fujita free volume theory(2). In that analysis, the free volume parameters were compared with the ones obtained from the study of viscosity data(3) of the same system (toluene - polyisobutylene). Also comparisons were made with the polymer free volume parameters reported in the literature which were obtained from viscoelastic(4) and other diffusion measurements.

In this study the self - diffusion coefficient data(1) of toluene in PIB are analysed using the Vrentas - Duda free volume theory(5-10). This theory is known to be able to describe the penetrant self - diffusion coefficient in both rubbery and glassy polymers. The theory introduces a number of parameters which have physical significance and furthermore they are not simply adjusted in order to achieve a good empirical fit of the diffusion data. Most of the parameters can be determined independently from sources other than diffusion studies, such as viscosity and $^{13}C\ T_1$ data. Thus it may be possible to predict(11) general diffusion behavior without the existence of any direct experimental data. However, quantitative predictions of D are not always possible and usually one to three adjustable parameters are needed to fit diffusion data. In addition Zielinski and Duda(11) have pointed out the utility of carbon-13 spin-lattice relaxation experiments in providing values for the parameters in the Vrentas-Duda theory and accordingly a detailed NMR study on pure PIB was completed prior to this study of penetrant translational diffusion.

The Vrentas - Duda theory is based on the Cohen - Turnbull result(12) showing that the mobility of a molecule in a pure liquid is related to the average free volume, v_f, per molecule through the following equation:

$$\ln m = E - \gamma v^* / v_f \qquad (1)$$

where γ is a numerical factor between 0.5 and 1, also known as overlap factor, that is introduced because a given free volume may be available to more than one molecule and v^* is the minimum volume of a hole that a molecule must find in its vicinity in order for it to move. According to Cohen and Turnbull molecules are resident in cages bound by their neighbors for the majority of the time. When a density fluctuation occurs and a hole of enough size opens within the molecular cage, the molecule jumps into the hole. Diffusional motion is considered to be translation of a molecule across the space within its cage and bulk diffusion then occurs as a result of redistribution of the free volume within the liquid. The above equation was derived under the assumption that redistribution of free volume (holes) at constant volume requires no change in energy. Equation (1) demonstrates that when the minimum volume of a hole that a molecule must find for a jump to occur is larger than the average free volume per molecule then the mobility of the penetrant is small. Conversely, when v^* is smaller than v_f then the molecule can jump to a neighbouring position and the mobility is high.

Vrentas - Duda(5) formulated their theory based on the following assumptions as stated(5, 13):

(i) V_f' is the free volume equal to the space not occupied by the actual molecules.

(ii) The free volume available to each jumping unit: solvent molecule or polymer segment, is equal to V_f' / N where N is the total number of solvent molecules plus polymer segments and V_f' is the total free volume of the solution.

(iii) The critical hole volume, v^*, of a jumping unit is equal to its intrinsic volume at zero Kelvin.

(iv) The partial specific volumes of the solvent and polymer are independent of composition i.e. there is no volume change on mixing and thermal expansion coefficients are given by their average values over the temperature range considered.

(v) As the temperature is increased, the increase in volume comes from the homogeneous expansion of the material due to the increasing amplitude of the anharmonic vibrations with temperature and from the formation of holes or vacancies which are distributed discontinuously throughout the material at any instant. The free space that is not occupied by the constituent molecules and is not associated with any holes or vacancies is called interstitial free volume. The energy for redistribution of the interstitial free volume is very large and this type of free volume therefore must be distributed uniformly among the molecules. The free volume associated with the discontinuous distribution of holes in the liquid is called the hole free volume. This free volume can be redistributed with no increase in energy.

To summarize the volume of a liquid can be divided into two parts: the volume occupied by the molecules of the liquid and the empty space between the molecules, designated as the free volume. Due to thermal fluctuations, part of the free volume is continuously redistributed, causing fluctuations in the local density. This free volume is called hole free volume. A molecule will translate through these fluctuating voids. According to the theory in order for a molecule to undergo a diffusing jump two things must happen: (i) a hole of sufficient size must appear next to the molecule and (ii) the molecule must possess enough energy to jump into the void. Thus the diffusion of a molecule is controlled by the probability that a hole of enough size will form in its vicinity and by the probability that the molecule will have enough energy to jump into this hole. For polymer - solvent systems above the glass transition temperature, the hole free volume is small and therefore the diffusion of the penetrant is mostly controlled by the probability of finding a hole of enough size in the vicinity of the penetrant molecule and by extension the size of that migrating molecule.

In this work the parameters of the Vrentas - Duda theory for the toluene - PIB system are determined from toluene self - diffusion data and compared with the ones obtained for other polymers. Also the Fujita free volume theory is known(14) to be identical to the Vrentas - Duda free volume theory under certain conditions, in accord with expectations. The polymer jumping unit of PIB is compared with the jumping units of other polymers as a function of their glass transition temperatures, using different polymer - solvent systems. The apparent activation energies for diffusion of different penetrants in PIB are also considered.

Experimental

The materials used for this study as well as the experimental pulse sequence and conditions are described in reference 1.

Interpretation

The self - diffusion of toluene in PIB was analysed via the Vrentas - Duda theory(5-10). According to this theory the self diffusion coefficient of a penetrant into a rubbery polymer is given by(5 - 10):

$$D_1 = D_0 \exp\left(\frac{-E}{RT}\right) \exp\left[\frac{-(\omega_1 V_1^* + \omega_2 \xi V_2^*)}{\omega_1 \left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T) + \omega_2 \left(\frac{K_{12}}{\gamma}\right)(K_{22} - T_{g2} + T)}\right] \quad (2)$$

where V_i^* is the specific critical hole free volume of component i required for a jump (i can be equal to 1 or 2; 1 for penetrant or solvent and 2 for polymer), ω_i is the mass fraction of component i, T_{gi} is the glass transition temperature of component i, D_0 is a constant pre-exponential factor, E is the energy per mole that a molecule needs to overcome attractive forces which constrain it to its neighbors and γ is an overlap factor (between 1/2 and 1) which is introduced because the same free volume is available to more than one molecule. K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are free volume parameters for the polymer.

The free volume parameters K_{11}, K_{21}, K_{12}, K_{22} are defined as follows(5):

$$K_{11} = V_1^0(T_{g1})[\alpha_1 - (1 - f_{H1}^G)\alpha_{c1}] \tag{3}$$

$$K_{21} = \frac{f_{H1}^G}{\alpha_1 - (1 - f_{H1}^G)\alpha_{c1}} \tag{4}$$

$$K_{12} = V_2^0(T_{g2})[\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}] \tag{5}$$

$$K_{22} = \frac{f_{H2}^G}{\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}} \tag{6}$$

$$f_{H1}^G = \frac{K_{11}K_{21}}{V_1^0(T_{g1})} \tag{7}$$

$$f_{H2}^G = \frac{K_{12}K_{22}}{V_2^0(T_{g2})} \tag{8}$$

where α_i is the thermal expansion coefficient for the equilibrium liquid component i, α_{ci} is the thermal expansion coefficient for the component i for the sum of the specific occupied volume and the specific interstitial volume, V_i^0 is the specific volume of the pure equilibrium component i and f_{Hi}^G is the fractional hole free volume of the component i at T_{gi}.

Finally, ξ is the ratio of molar volume of a solvent jumping unit to the molar volume of a polymer jumping unit. The parameter ξ can be a measure of the molar volume of the solvent jumping unit. When the entire solvent molecule performs a jump during the process of the self - diffusion, then the molar volume of the solvent jumping unit is equal to the molar volume of the liquid solvent. In some cases the solvent jumping unit constitutes only a portion of the molecule and hence the molar volume of the jumping unit is smaller than the molar volume of the liquid solvent. The solvent jumping unit is always smaller than or equal to the molar volume of the liquid solvent. Also the size of the solvent jumping unit that undergoes segment wise diffusion, depends on the characteristics of the polymer through which it is diffusing(15).

There are nine independent parameters in equation (2), D_0, E, ξ, K_{11}/γ, $K_{21} - T_{g1}$, K_{12}/γ, $K_{22} - T_{g2}$, V_1^*, V_2^* that need to be determined. However, most of them can be determined from viscosity data or sources other than diffusion data and in favorable cases all of them could conceivably be set from other data.

The two critical volumes V_1^*, and V_2^*, represent the minimum specific hole free volumes required to allow a solvent and polymer molecule respectively to take a diffusive jump and are estimated as the specific volumes of the solvent and polymer at temperature T = 0 K. Group contribution methods developed by Sugden(16) and Biltz(17) are used for the estimation of the molar volumes at 0 K. Those methods were summarised by Haward in reference (18). For the system under study these parameters are(11): $V_1^* = 0.917$ (cm^3 / gr) and $V_2^* = 1.004$ (cm^3 / gr).

The polymer free volume parameters K_{12}/γ, $K_{22} - T_{g2}$, can be estimated either from polymer viscosity data or from the WLF parameters through the equations(6, 11):

$$\frac{\gamma V_2^*}{K_{12}} = 2.303(C_{12}^g)(C_{22}^g) \tag{9}$$

$$K_{22} = (C_{22}^g) \tag{10}$$

where the "g" on the exponent means that the reference temperature for the WLF parameters is the glass transition temperature. NMR studies of the ^{13}C spin - lattice relaxation time as a function of temperature and Larmor frequency can be useful(19) for determining the WLF coefficients and for PIB quite a few different sets of WLF coefficients have been reported in the literature:

(1) From reference (4), from viscoelastic measurements $C_{12}^g = 16.07$, $C_{22}^g = 107.4$ K and we obtain:

$$K_{12}/\gamma = 2.526\ 10^{-4}\ (\text{cm}^3/\text{gr K}), \quad K_{22} - T_{g2} = -97.6\ \text{K}.$$

(2) From reference (11) from viscosity data $C_{12}^g = 16.63$, $C_{22}^g = 104.4$ K and:

$$K_{12}/\gamma = 2.51\ 10^{-4}\ (\text{cm}^3/\text{gr K}), \quad K_{22} - T_{g2} = -100.6\ \text{K}.$$

(3) From a detailed NMR study(20) of the ^{13}C spin - lattice relaxation times for neat PIB as a function of temperature and Larmor frequency we obtain (for $C_{12}^g = 9.33$, $C_{22}^g = 107.4$ K):

$$K_{12}/\gamma = 4.351\ 10^{-4}\ (\text{cm}^3/\text{gr K}), \quad K_{22} - T_{g2} = -97.4\ \text{K}.$$

The solvent free volume parameters K_{11}/γ and $K_{21} - T_{g1}$, can be estimated from equations similar to equations (9) and (10) from WLF coefficients. Viscosity data alone for the solvent can provide all four parameters(11) (K_{11}/γ, $K_{21} - T_{g1}$, D_0 and E), however the fitting in this case is uncritical and cannot yield a unique set of parameter values. The only way to overcome this problem is to assume $E = 0$. With this assumption a different set of parameters is obtained from those assuming $E \neq 0$, and these parameters give better predictions for the diffusion coefficient of a penetrant into a polymer(21). The values of the parameters that are reported in the literature are:

(1) From reference (19), for toluene from viscosity data, $C_{11}{}^{g} = 10.75$, $C_{21}{}^{g} = 23.6$ K which give ($T_{g1} = 117$ K):

$$K_{11}/\gamma = 1.569\ 10^{-3}\ (\mathrm{cm}^3 / \mathrm{gr\ K}), \quad K_{21} - T_{g1} = -93.4\ \mathrm{K}.$$

(2) From reference (19), for toluene from NMR data, $C_{11}{}^{g} = 6.64$, $C_{21}{}^{g} = 34.51$ K which give ($T_{g1} = 117$ K):

$$K_{11}/\gamma = 1.738\ 10^{-3}\ (\mathrm{cm}^3 / \mathrm{gr\ K}), \quad K_{21} - T_{g1} = -82.49\ \mathrm{K}.$$

(3) From reference (22), from viscosity data for toluene:

$$K_{11}/\gamma = 2.21\ 10^{-3}\ (\mathrm{cm}^3 / \mathrm{gr\ K}), \quad K_{21} - T_{g1} = -103\ \mathrm{K}.$$

(4) From reference (9), from viscosity data, for toluene:

$$K_{11}/\gamma = 1.57\ 10^{-3}\ (\mathrm{cm}^3 / \mathrm{gr\ K}), \quad K_{21} - T_{g1} = -90.5\ \mathrm{K}.$$

(5) From reference (23) from viscosity data for toluene, $C_{11}{}^{g} = 15.8$, $C_{21}{}^{g} = 11.4$ K which give ($T_{g1} = 114$ K):

$$K_{11}/\gamma = 2.211\ 10^{-3}\ (\mathrm{cm}^3 / \mathrm{gr\ K}), \quad K_{21} - T_{g1} = -102.6\ \mathrm{K}.$$

(6) From reference (11), from viscosity data:

$$K_{11}/\gamma = 1.45\ 10^{-3}\ (\mathrm{cm}^3 / \mathrm{gr\ K}), \quad K_{21} - T_{g1} = -86.32\ \mathrm{K}.$$

The differences in the free volume parameters are due to experimental errors in the viscosity data and to the uncertainty in the fitting parameters.

The pre-exponential factor D_0, is considered to be solvent dependent(11). In order to verify if this is true, the D_0 value obtained from the analysis of the viscosity data of pure toluene is used to describe the diffusion of toluene in different polymers. It has been found(11) that a specific value of D_0 adequately describes the transport of toluene in various polymers (polystyrene, polyvinyl acetate, polymethyl methacrylate). A recent report(11) shows that the value of D_0 associated with the free volume parameters $K_{11}/\gamma = 1.45\ 10^{-3}$ (cm^3 / gr K) and $K_{21} - T_{g1} = -86.32$ K, is $4.82\ 10^{-4}$ cm^2 / sec. It must be noted that if a different set of values for K_{11}/γ and $K_{21} - T_{g1}$ are used, then a different number for D_0 should be used also.

The last parameter left to be determined, is ξ: the ratio of the molar volume of a solvent jumping unit to the molar volume of a polymer jumping unit. For the case of small penetrants / solvents such as benzene, methane etc. that move as single units, ξ is defined as :

$$\xi = \frac{V_1^0(0)}{V_{2j}} = \frac{M_1 V_1^*}{M_{2j} V_2^*} \tag{11}$$

where $V_1{}^0(0)$ is the solvent molar volume, V_{2j} is the polymer jumping unit volume, M_1 is the molecular weight of the entire solvent and M_{2j} is the molecular weight of the polymer jumping unit. It has been shown(24) that $(\gamma V_2{}^* \xi / K_{12})$ depends linearly on the solvent molar volume (at 0 K) and the resulting straight line passes through the origin when the solvent moves as a single unit:

$$\frac{\gamma V_2^* \xi}{K_{12}} = \beta V_1^0(0) \tag{12}$$

Equation (12) suggests (using the definition of ξ above) that the size of the polymer jumping unit doesn't depend on the solvent and is polymer dependent. Therefore, if β is known for a particular polymer, the value of ξ for any solvent in that polymer can be calculated accurately, if the solvent diffuses as a single unit. In order to estimate β for a polymer, a lot of diffusion data of different penetrants must be studied first, in order to extract the values of ξ and then make the plot of $(\gamma V_2{}^* \xi / K_{12})$ vs $V_1{}^0(0)$ (the slope will be β). After β is known, predictions of the diffusion coefficient of a penetrant in the particular polymer can be made. For polyisobutylene the value of β is not known and thus the parameter ξ will be the only parameter that will be floated in order to calculate the diffusion coefficient of toluene in polyisobutylene.

In order to fit the diffusion data of toluene in PIB as a function of concentration, the parameters shown in Table 1 were used. Since all the toluene and polymer free volume parameters mentioned above are close to each other, the actual choice of a parameter set is somewhat arbitrary and doesn't significantly change the quality of the fit.

As a result of the fit, ξ was found to be equal to 0.892 ± 0.08. The experimental self - diffusion coefficients of toluene in PIB along with the fitting curves (solid lines) are shown as a function of temperature and concentration in Figures 1(a) and 1(b).

Discussion

The fitting of the concentration dependence of the self - diffusion of toluene in PIB has determined a value for ξ which is 0.892 ± 0.08. This value corresponds to a polymer jumping unit of molecular weight 94.3 as derived from equation (11) when the toluene moves as a single unit. This value is close to the molecular weight of toluene ($M_1 = 92.13$). It is thus seen that the size of the polymer jumping unit is approximately the same as the size of the penetrant jumping unit. In view of this result, it would be appropriate to expect that both polymer and penetrant jumping units would require approximately the same minimum hole size necessary for a diffusion jump. It has been shown(5) previously that both Fujita and Vrentas - Duda free volume theories can be used when the molecular weights of the two jumping units are the same. As indicated in reference (14), the two theories are identical when the following condition is true:

$$\frac{\xi V_2^*}{V_2^0} = \frac{V_1^*}{V_1^0} \tag{13}$$

and when B_d (minimum hole size required for a given molecule to permit a displacement, according to Fujita theory(2)) is defined as:

$$B_d = \frac{\gamma V_1^*}{V_1^0} \tag{14}$$

This can be done by rewriting equation (1) as:

$$\ln\left(\frac{D_1}{D_1(0)}\right) = \frac{\phi_1\left(\frac{\xi V_2^* f_1}{V_2^0 \gamma} - \frac{V_1^* f_2}{V_1^0 \gamma}\right)}{\left[\frac{f_2^2}{\gamma^2} + \phi_1 \frac{f_2}{\gamma}\left(\frac{f_1}{\gamma} - \frac{f_2}{\gamma}\right)\right]} \tag{15}$$

where $D_1(0)$ is the self - diffusion coefficient of the penetrant at the limit $\omega_1 = 0$, V_i^0 is the specific volume of pure component i at the temperature of interest, V_i^* is the specific critical hole free volume of component i required for a jump, ϕ_1 is the volume fraction of the solvent and f_i is the fractional hole - free volume of pure component i at the temperature of interest and the f_i's are given by:

$$f_1 = \frac{(K_{21} + T - T_{g1})K_{11}}{V_1^0} \qquad f_2 = \frac{(K_{22} + T - T_{g2})K_{12}}{V_2^0} \tag{16}$$

Using equations (13) and (14), equation (15) can be written as:

$$\ln\left(\frac{D_1}{D_1(0)}\right) = \frac{B_d (f_1 - f_2)\phi_1}{f_2^2 + f_2 (f_1 - f_2)\phi_1} \tag{17}$$

Equation (17) is identical to the equation derived by Fujita(2). For $\xi = 0.892$, $V_2^* = 1.004$ cm^3 / gr, $V_1^* = 0.917$ cm^3 / gr, $V_2^0 = 1.091$ cm^3 / gr, and $V_1^0 = 1.154$ cm^3 / gr we find that the left hand side of equation (13) is equal to 0.821 and the right hand side of equation (13) is equal to 0.794. Therefore we see that since the two ratios are close, either of the two theories can be used for the toluene - polyisobutylene system. Thus it is no surprise that both approaches accurately describe the temperature and concentration dependence of the self - diffusion constant.

Also as it has been pointed out(14) the free volume parameters of the Fujita theory can be determined from the free volume parameters of the Vrentas - Duda theory if they are known. This is done with the help of the following equations:

$$\frac{f_p(T)}{B_d} = \frac{f_2(f_1 - f_2)}{\gamma^2 F} \qquad \frac{f_s(T)}{B_d} = \frac{f_p(T)}{B_d}\frac{f_1}{f_2} \qquad (18)$$

where f_1 and f_2 are given by equation (16) and

$$F = \frac{\xi V_2^* f_1}{V_2^0 \gamma} - \frac{V_1^* f_2}{V_1^0 \gamma} \qquad (19)$$

V_i^0 is the specific volume of pure component i, $f_p(T)$ is the average fractional free volume of pure polymer (as defined in Fujita theory(2)), $f_s(T)$ the fractional free volume of solvent (toluene) in the solution at the limit of zero toluene concentration (as defined by Fujita for the toluene - PIB system(3)) and B_d a constant that represents the minimum hole size required for a given molecule to permit a displacement, (as defined in Fujita theory(2)).

Using equations (16), (18) and (19) and the parameters from Table 1, the Fujita parameters can be predicted. Using T = 298 K, and the free volume parameters (Table 1) we obtain:

$$\frac{f_p(298K)}{B_d} = 0.096\ ; \qquad \frac{f_s(298K)}{B_d} = 0.32\ . \qquad (20)$$

These values are close to the ones (for T = 298 K, $f_p(T) / B_d = 0.08735$ and $f_s(T) / B_d = 0.273$) obtained from the actual fit using the Fujita theory (Paper I of this series). This verifies the correspondence of the two theories when the conditions described by equations (13) and (14) are true and demonstrates that it is possible to determine the Fujita free volume parameters if the Vrentas - Duda free volume parameters are known.

The results obtained here for ξ from the PIB - toluene system can be compared with the data on a number of other polymers. If equation (11) is multiplied and divided by M_{2mono}, the molecular weight of the polymer monomer unit, it can be rewritten as:

$$\xi = \frac{M_{2mono}}{M_{2j}} \frac{V_1^0(0)}{V_2^* M_{2mono}} \qquad (21)$$

In Figure 2 a plot of ξ vs $V_1{}^0(0) / V_2{}^* M_{2mono}$ is shown for different polymers. The values of $V_1{}^0(0) / V_2{}^* M_{2mono}$ were calculated from Tables 2 and 3 from reference (11) where the $V_1{}^0(0)$, M_{2mono}, M_{2j}, $V_2{}^*$ are given for different polymers and solvents. For each polymer shown in Figure 2, the parameters M_{2mono}, M_{2j} and $V_2{}^*$ are given in Table 3 in reference (11). Then from Table 2 (in reference (11)) the values of $V_1{}^0(0)$ are taken for different solvents. Those solvents are: acetone, benzene, carbon tetrachloride, chloroform, ethyl benzene, n-hexane, methyl acetate, methylene chloride, n-octane, n-pentane, tetrahydrofuran, toluene, o-xylene and cyclohexane. Thus for every polymer the value of ξ is calculated from equation (12), for every solvent mentioned above, since the values of β, for some polymers, are known and reported in Table 3 in reference 11. The values of ξ for polybutadiene were calculated using Table 2 from reference (11) and the free volume parameters reported in reference (25). The values of ξ for polyisobutylene were calculated using Table 2 from reference (2) and the free volume parameters showed in the Table 1 above. The values reported here for PIB and polybutadiene are estimates from the currently available data obtained from a single polymer - penetrant system; and thus the uncertainty is large. Better estimates for ξ, β and M_{2j} could be made when additional diffusion data are available.

The parameter β is accurately known for polystyrene (PS), poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(vinyl acetate) (PVAc) because of extensive prior studies(11).

Figure 2, plotted according to equation (21), shows that most of the data have a slope about $M_{2mono} / M_{2j} = 2 / 3$ which indicates that the size of the polymer jumping unit is 1.5 times as large as the monomer segment. PMMA seems to be an exception; its jumping unit is almost two times larger than the monomer unit. For polyisobutylene M_{2j} / M_{2mono} is 1.68 which is close to the typical value of 1.5. From equation (11) it can also be concluded that for the same solvent, as the polymer jumping unit becomes larger, the value of ξ becomes smaller. This implies faster diffusion for a larger polymer jumping unit which seems inconsistent though the complex dependency of D on a number of parameters given by equation (2) makes it difficult to predict trends for a single parameter.

In Figure 3 the molecular weight of the polymer jumping unit is plotted as a function of the polymer monomer molecular weight . The solid line has a slope of 1.5. This plot shows more clearly that the polymer jumping unit is approximately 1.5 times polymer monomer molecular weight. Polyisobutylene is consistent with the other polymers in this plot. Of course more data must be collected for more polymers in different solvents in order to be able to conclude that the molecular weight of the polymer jumping unit is in general 1.5 times the molecular weight of the polymer monomer unit.

To try to relate the size of the polymer jumping unit with the chain stiffness(11), a plot of the polymer glass transition temperature vs the molar volume of the polymer jumping unit is made (Figure 4). The data are derived from equation (11) using the parameters given in Tables 2 and 3 in reference (11), while toluene was chosen arbitrarily as the penetrant. Again the data for the polybutadiene were taken from reference (25). The validity of the relationship of V_{2j} with the polymer glass transition temperature reported in reference (11)

$$V_{2j}\ (\mathrm{cm}^3/\mathrm{mole}) = 0.6224\ T_{g2}\ (\mathrm{K}) - 86.95 \qquad (22)$$

is not evidenced when two new data points were added; that of PIB and that of polybutadiene (parameters taken from reference (25)). Therefore it seems that additional diffusion data are required in order to have a better understanding about the relationship between the volume of the polymer jumping unit and the polymer glass transition temperature.

A constant temperature independent activation energy for diffusion can be defined relative to the Arrhenius equation:

$$D = D_0 \exp(-E^* / R\,T) \qquad (23)$$

by taking the derivative of lnD with respect to (1 / T) and multiplying by (-R). That is, in general one can define (4, 24):

$$E_D = -R\frac{\partial \ln D}{\partial(\frac{1}{T})} = RT^2\frac{\partial \ln D}{\partial T} \qquad (24)$$

where when lnD varies linearly with (1 / T), then $E_D = E^*$. However when lnD does not vary linearly with (1 / T), then the last equation formally defines a temperature dependent "activation energy".

Equation (2) can be rewritten at the limit of zero penetrant concentration ($\omega_1 = 0$ and $\omega_2 = 1$) and for E = 0:

$$\ln D = \ln D_0 - \frac{\gamma V_2^* \xi}{K_{12}(K_{22} - T_{g2} + T)} \qquad (25)$$

Therefore the apparent activation energy for diffusion in the limit of zero penetrant concentration, which is obtained by equations (24) and (25), is related to the free volume parameters by the expression(4 - 5, 24, 26):

$$E_D = \frac{RT^2\left(\frac{\gamma V_2^* \xi}{K_{12}}\right)}{(K_{22} + T - T_{g2})^2} \qquad (26)$$

Using the parameters shown in Table 1, the apparent activation energy for diffusion at T = 298 K is estimated to be about 37.8 kJ / mole. The activation energy as a function of temperature is shown in Figure 5. The values obtained are close to the values reported in reference (20) for segmental motion of PIB, but lower than the values obtained from the Fujita analysis of penetrant diffusion(1) (paper 1 in this series).

From equation (26), if the apparent activation energy for diffusion is known, then the value of the expression ($\gamma V_2^* \xi / K_{12}$) can be extracted and then ξ obtained. From the Fujita interpretation, it was found that the apparent activation energy at the limit of zero toluene concentration is 58.9 kJ / mole at 298 K. Using this determination, the value of ($\gamma V_2^* \xi / K_{12}$) is found to be about 3204 K. This value is compared with other values obtained for other penetrants in polyisobutylene(26) in Figure 6. The values for ($\gamma V_2^* \xi / K_{12}$) and the corresponding ξ, for the different polymer - penetrant systems, are shown in Table 2. The data were taken from reference (26), except for the point that corresponds to the toluene - PIB system. The ξ 's were extracted using $V_2^* = 1.004$ (cm^3 / gr) and $K_{12}/\gamma = 2.51\ 10^{-4}$ cm^3 / gr K (which was obtained from viscosity data) for all the penetrant - polymer systems. For the toluene - PIB system, in order to be consistent with the rest of the data presented in the graph, the value of $K_{12}/\gamma = 2.51\ 10^{-4}$ cm^3 / gr K was used in the calculation of ($\gamma V_2^* \xi / K_{12}$) instead of $K_{12}/\gamma = 4.351\ 10^{-4}$ cm^3 / gr obtained from the NMR data. If $K_{12}/\gamma = 4.351\ 10^{-4}$ cm^3 / gr is considered then ξ is found to be 1.38 for the toluene - PIB system. This last estimate of ξ is very approximate and has a large error because of the error in the estimation of the activation energy and the uncertainty in the K_{12}/γ parameter. The value $\xi = 0.892$ is more accurate since it was extracted directly from the diffusion data and implies that toluene is moving as a single unit in accord with recent conclusions(11, 14, 19, 21). From Figure 6 it also can be seen that the eight solvents (filled circles) that may be expected to move as single units deviate from a straight line in contradiction to equation (12). This deviation may be due to experimental error since primitive diffusion data from different laboratories are being used. Another possibility is that the energy, E per mole, that a molecule needs in order to overcome the attractive forces which constrain it to its neighbors makes a significant contribution to the apparent activation energy, E_D, for diffusion and therefore equation (26) should be modified as$^{(26)}$:

$$E_D = E + \frac{RT^2\left(\frac{\gamma \hat{V}_2^* \xi}{K_{12}}\right)}{(K_{22} + T - T_{g2})^2} \tag{27}$$

Assuming that E = 6000 cal / g mole, a recalculation of $(\gamma V_2^* \xi / K_{12})$ from equation (27) shows that the points under question can be reasonably represented by a straight line according to equation (12), as it is demonstrated in reference (26).

However, the assumption that E is different from zero, introduces one more parameter into the fitting process. This would increase the uncertainty of the fitting parameters by a significant percentage. Also, this would have an effect on the values of the parameters D_0, K_{11} / γ and $K_{21} - T_{g1}$ which are obtained from the analysis of viscosity and specific volume data for the pure solvent. If E is included, a four parameter regression (D_0, E, K_{11} / γ and $K_{21} - T_{g1}$) would be required to fit the temperature dependence of the viscosity and specific volume data$^{(21)}$. This would make it very difficult to produce fits which converge to a single set of parameters describing the viscosity and specific volume data$^{(21)}$. Thus the assumption that E is different from zero would increase the uncertainty in D_0, K_{11} / γ and $K_{21} - T_{g1}$. Also it has been demonstrated$^{(21)}$ that the Vrentas - Duda theory is by far more successful in predicting the self - diffusion coefficient of the penetrant in different polymer - solvent systems (toluene - polystyrene; ehtylbenzene - polystyrene; benzene - polystyrene) when the assumption of E = 0 is employed. Thus it is our feeling that the deviation from a straight line of the eight points (filled circles in Figure 6) is due to experimental error and not due to the neglect of E in equation (27).

Another characteristic that is seen in Figure 6 is the existence of a ceiling value of $(\gamma V_2^* \xi / K_{12})$ and therefore of E_D for large penetrant molecules. This seems to be in contradiction with the free volume theory as expressed by equation (26). For a given polymer, if the size of the penetrant increases, ξ increases and thus E_D increases. Thus free volume theory predicts that E_D should increase indefinitely as the size of the penetrant molecule increases. However the apparent activation energy E_D does not necessarily increase with an increase in the size of an entire penetrant molecule if the penetrant molecule moves in a segment wise manner, i.e. if the penetrant jumping unit is a portion of the molecular unit. Therefore the ceiling value of ($\gamma V_2^* \xi$ / K_{12}) in Figure 6 for the penetrants n-dodecane, n-hexadecane, 1,1-diphenylethane and 2,2,5-trimethyl hexane may be an indication of segment wise motion for these penetrants. This would not be very surprising because of the size and structure of these molecules.

Conclusions

The Vrentas-Duda free volume interpretation of the diffusion of toluene in PIB is of comparable quality to the Fujita interpretation presented in the preceding paper. Indeed, this should be so since the two theories coincide when the size of the jumping unit of the polymer matches the size of the penetrant as it does in this system. It is informative to consider the parameters of the Vrentas-Duda theory for this system relative to other systems as was presented in various ways in the Discussion section. Nevertheless, both free volume interpretations seem equally appropriate and informative for this system.

It would be desirable if the ideas from free volume concepts were able to shed some light on the rather unique behaviour of PIB relative to other polymers. In particular the unusual slow diffusion exhibited by PIB with respect to a variety of penetrants might be expected to be reflected in the value of certain free volume parameters. This is seen in the fact that the WLF parameters: c_1 and c_2, are considerably different from most other polymers, which can be adequately represented by the so-called universal values(4). The parameter α, the fractional free volume expansion factor, is considerably smaller than is typical for other polymers and does give some physical insight into the origin of the lower free volume at temperatures above the glass transition. This parameter is derived directly from the Fujita analysis(1). The Vrentas-Duda parameters, though useful in their potential for predictability, do not appear to yield any physical insight into uniqueness of PIB.

Acknowledgement

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Table 1

Values of parameters for PIB / Toluene systems.

V_1^* (cm^3 / gr)	0.917
V_2^* (cm^3 / gr)	1.004
K_{11} / γ (cm^3 / gr K)	1.45 10^{-3}
K_{12} / γ (cm^3 / gr K)	4.351 10^{-4}
$K_{21} - T_{g1}$ (K)	-86.32
$K_{22} - T_{g2}$ (K)	-97.6
ξ	0.892 ± 0.08
D_0 (cm^2 / sec)	4.82 10^{-4}
E (kcal / mole)	0
M_1	92.13
V_1^0 (cm^3 / gr mole)	84.48
T_{g1} (K)	117
M_{2mono}	56.04
C_{12}^g	9.33
C_{22}^g (K)	107.4
T_{g2} (K)	205

Table 2

Parameter ξ obtained from equation (26) for different penetrants in PIB.

Penetrant	$\gamma V_2^* \xi / K_{12}$ (K)	ξ
1. Hydrogen	1730	0.433
2. Oxygen	2460	0.616
3. Nitrogen	2660	0.667
4. Carbon dioxide	2660	0.667
5. n - Butane	3820	0.958
6. iso - Butane	4010	1.00
7. n - Pentane	3660	0.918
8. iso - Pentane	4150	1.04
9. Neopentane	4120	1.03
10. n - Dodecane	3620	0.907
11. n - Hexadecane	3620	0.908
12. 1,1-Diphenylethane	3780	0.946
13. Cyclohexane	3580	0.897
14. 2,2,5-Trimethylhexane	3910	0.981
15. Toluene	3204	0.801

Figure Captions

Figure 1(a) and 1(b): Diffusion coefficient of toluene in PIB as a function of concentration at different temperatures. Solid lines represent diffusion coefficients calculated from equation (2)..

Figure 2: A comparison of M_{2j} and M_{2mono} as demonstrated by equation (20) for various polymers: polystyrene (PS), poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(vinyl acetate) (PVAc), polyisobutylene (PIB), polybutadiene (PB). The solid line indicates that the molecular weight of the polymer jumping unit is 1.5 times as large as the molecular weight of the monomer unit. Various points of the same marker mean different solvents. Those solvents are: acetone, benzene, carbon tetrachloride, chloroform, ethylbenzene, n-hexane, methyl acetate, methylene chloride, n-octane, n-pentane, tetrahydrofuran, toluene, o-xylene and cyclohexane.

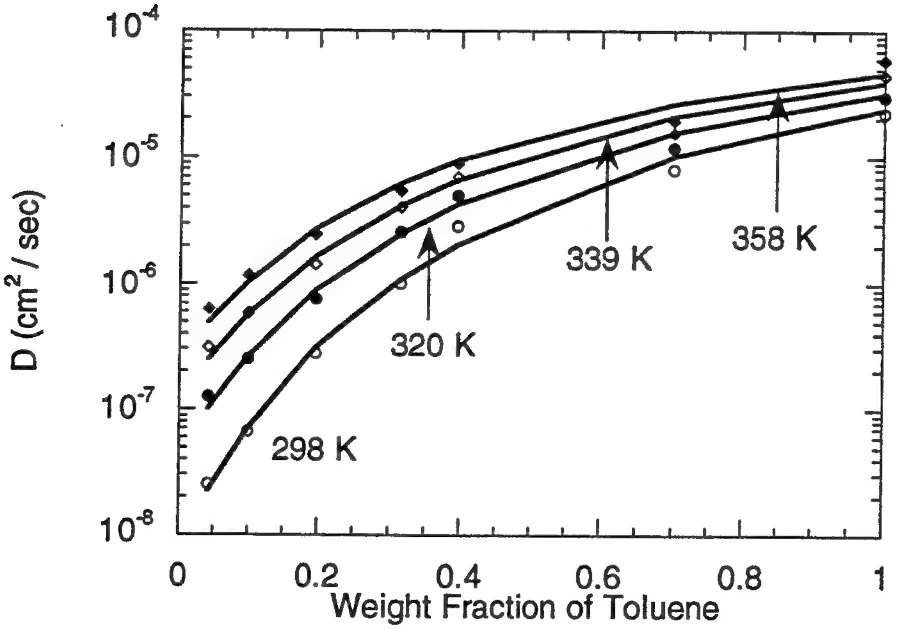
Figure 3: The molecular weight of the polymer jumping unit M_{2j} as a function of M_{2mono} the molecular weight of the polymer monomer unit. polystyrene (PS), poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEM) and poly(vinyl acetate) (PVAc), polyisobutylene (PIB), polybutadiene (PB). The solid line has a slope 1.5.

Figure 4: Polymer glass transition temperature vs the molar volume of the polymer jumping unit; polystyrene (PS), poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), and poly(vinyl acetate) (PVAc), polyisobutylene (PIB), polybutadiene (PB), cis - 1, 4 - poly(isoprene) (PI), poly(styrene - butadiene) (SB).

Figure 5: The activation energy for diffusion for the PIB - toluene system as a function of temperature in the limit of zero penetrant concentration.

Figure 6: ($\gamma V_2^* \xi / K_{12}$) vs Molar volume of solvent at 0 K for polyisobutylene solvent systems. Numbers designating solvents correspond to those in Table 3. Solid circles represent solvents which might be expected to move as single units and open circles represent solvents that may indicate a segmentwise motion. Data and graph were taken from reference (20). The rhombus represents toluene using parameters were taken from this work.

fig 1a


10^-4
10^-5
10^-6
10^-7
10^-8
D (cm^2 / sec)
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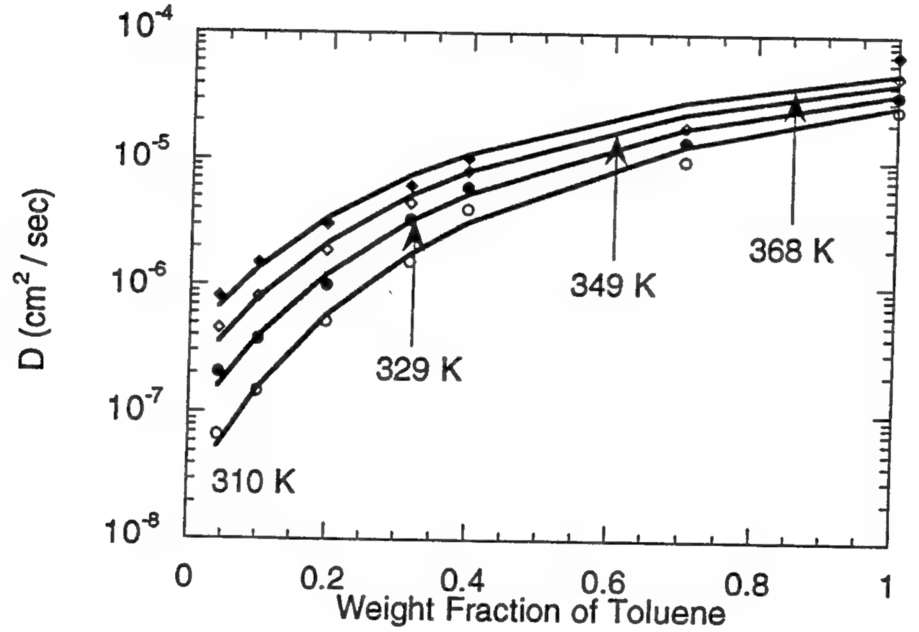
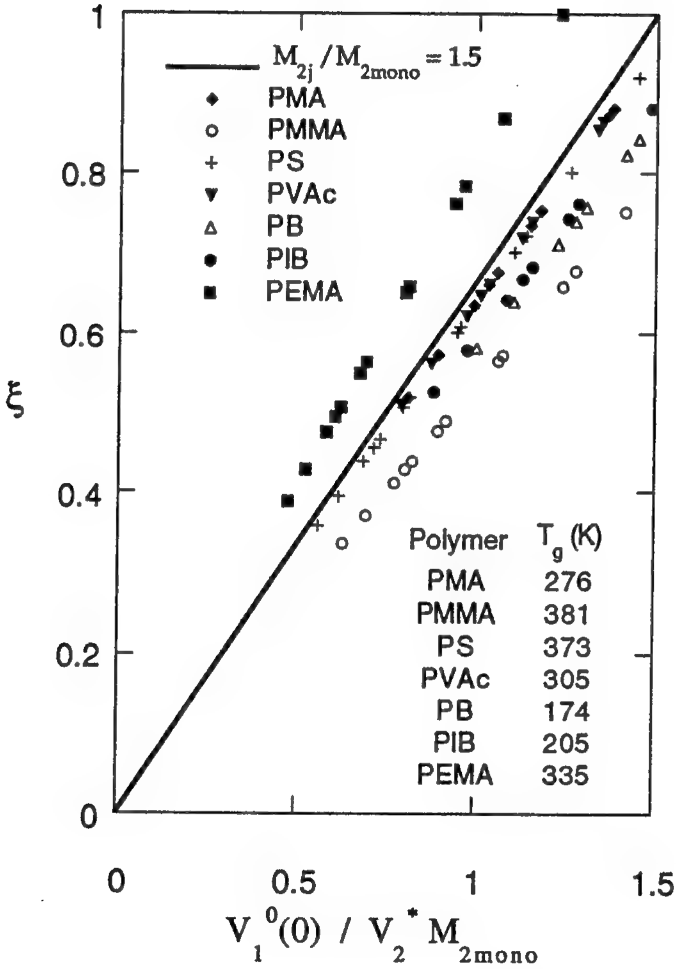
0.2
0.4
0.6
0.8
1
Weight Fraction of Toluene
298 K
320 K
339 K
358 K

fig 1h



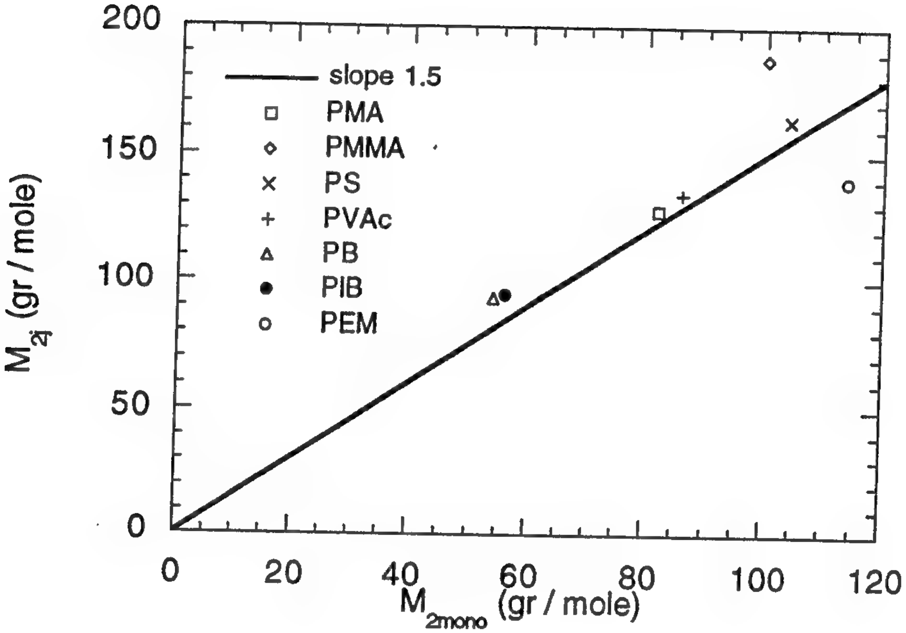
10^-4
10^-5
10^-6
10^-7
10^-8
D (cm^2 / sec)
0
0.2
0.4
0.6
0.8
1
Weight Fraction of Toluene
310 K
329 K
349 K
368 K

fig 2



Polymer	T_g (K)
PMA	276
PMMA	381
PS	373
PVAc	305
PB	174
PIB	205
PEMA	335

fig 3


slope 1.5
PMA
PMMA
PS
PVAc
PB
PIB
PEM
200
150
100
50
0
0
20
40
60
80
100
120
M_{2j} (gr / mole)
M_{2mono} (gr / mole)

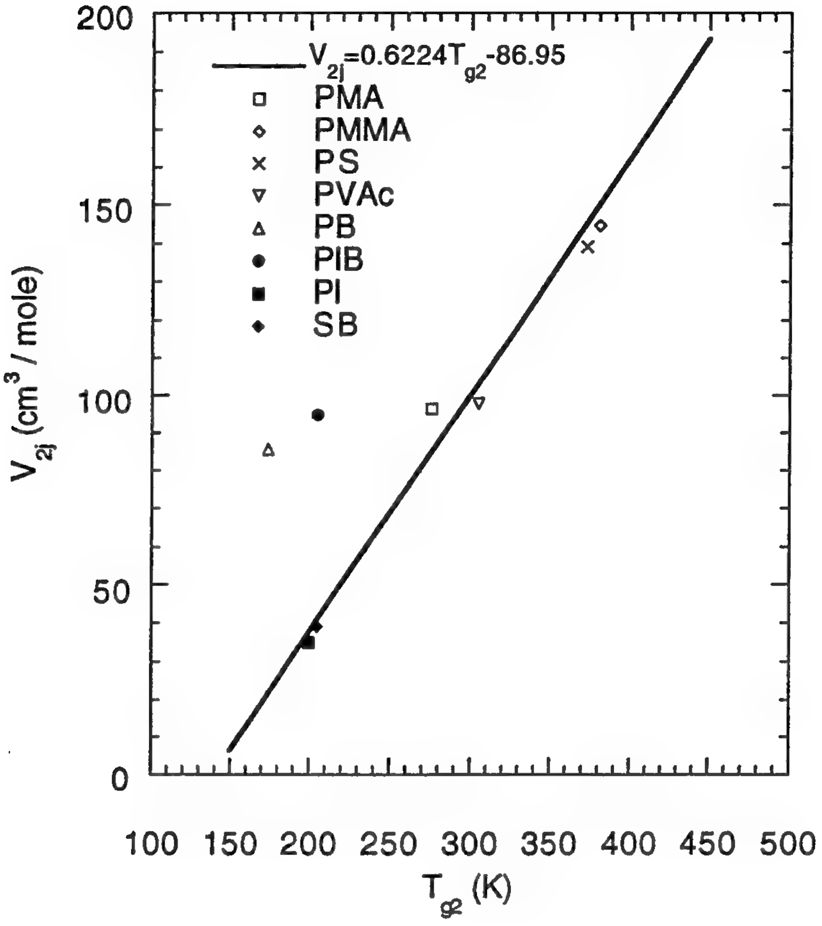
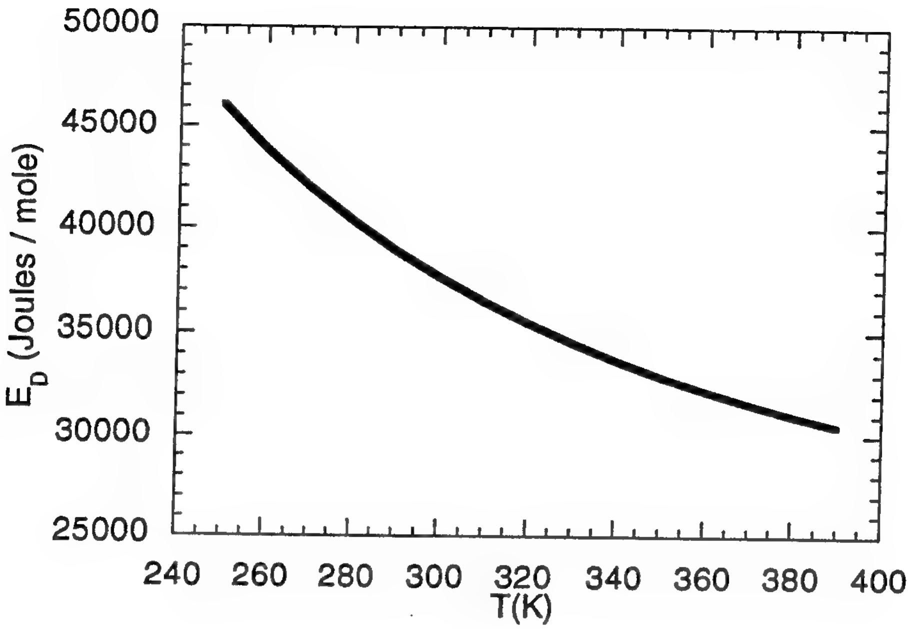

200
150
100
50
0
100 150 200 250 300 350 400 450 500
V_{2j} (cm^3 / mole)
T_{g2} (K)
$V_{2j}=0.6224T_{g2}-86.95$
□ PMA
◇ PMMA
× PS
▽ PVAc
△ PB
● PIB
■ PI
◆ SB

fig 4

fig 5


50000
45000
40000
35000
30000
25000
E_D (Joules / mole)
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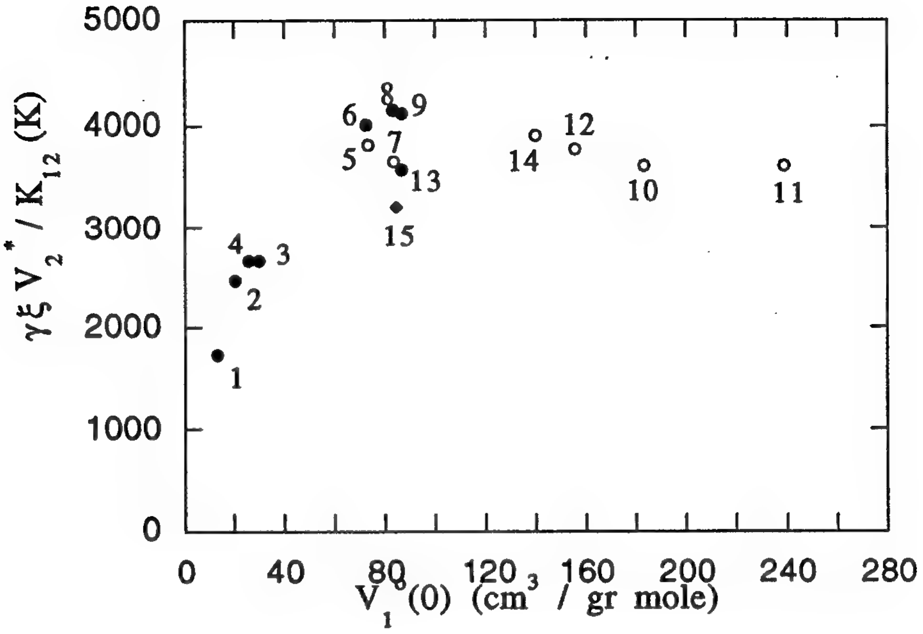
260
280
300
320
340
360
380
400
T(K)

fig 6


5000
4000
3000
2000
1000
0
0
40
80
120
160
200
240
280
$\gamma\xi V_2^* / K_{12}$ (K)
$V_1^o(0)$ (cm^3 / gr mole)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

A Nuclear Magnetic Resonance Study of Toluene - Polyisobutylene Solutions. (III) Spin-Lattice Relaxation: Rotational and Segmental Motion.

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Abstract

The spin - lattice relaxation times are determined for the methylene carbon of polyisobutylene (PIB), as well as for the ortho carbon of toluene in toluene - polyisobutylene solutions. The Hall - Helfand correlation function combined with restricted anisotropic rotational diffusion was used to treat the T_1 data of the methylene carbon of PIB. A simple exponential correlation function was used to describe the local motion of toluene in the solutions which falls in the extreme narrowing limit for the solutions studied. Both models described satisfactorily the temperature and field dependence of the spin - lattice relation times. From the temperature dependence of the correlation times for the polymer segmental motion, the free volume of the solution at each concentration is extracted and compared with the values obtained from previous studies of the translational motion of the toluene penetrant. The free volume values extracted from the T_1 data for the methylene carbon of PIB and the self - diffusion data for the toluene were found to be in substantial agreement. The interrelationship of the timescale of segmental motion of the polymer and the translational diffusion of the toluene was also examined and it was found that the two types of motion seem to be correlated in high polymer concentrated solutions. The toluene reorientational motion was found to be much faster than both the polymer segmental motion and the toluene translational diffusion leading to the conclusion that the toluene reorientational motion is uncoupled from these two motions.

Keywords: Segmental motion, Chain Dynamics, Polyisobutylene, Toluene, Hall - Helfand, NMR, Free Volume.

Introduction

Transport through polymers is a subject that has attracted interest during the past three decades because of the applications in medicine, biology and industry. The increased number of challenges that practitioners are faced in industry and applied chemistry has increased the need to find and understand more about the mechanisms that take place in a polymer when a penetrant molecule diffuses through the polymer matrix.

Numerous diffusion studies have been reported in the literature(1-5) and it has been found and demonstrated(6-9) by many researchers that free volume governs the transport of a penetrant through a polymer matrix. Numerous studies(10-13) have also described the behavior of a polymer in solution i.e. when the latter is in contact with a penetrant. A variety of models(10-15) that describe the segmental motion of a polymer in the bulk, well above the glass transition temperature, have been reported in the literature. In general, the same models can describe the segmental motion of the polymer in solution(16).

In order to obtain a better understanding about the mechanisms of transport in rubbery polymers it is necessary to study the overall translational and rotational motions of the penetrant as well as the local segmental motion of the polymer. To accomplish this for the toluene-PIB system, the self - diffusion coefficients of toluene in polyisobutylene (PIB) solutions were determined and analyzed as a function of temperature and concentration using the two most common free volume theories, namely the Fujita(6) and the Vrentas - Duda(7-9) theories, in the two previous papers(17-18) in this series. In those two papers the free volume parameters of the toluene - PIB solutions were determined from diffusion and compared with the ones obtained from viscosity data of the same solutions. Also, the Fujita theory was compared(18) with the Vrentas - Duda theory.

In this present work the local segmental motion of the polymer and the reorientational motion of the penetrant / solvent are determined using ^{13}C T_1 NMR measurements. Previous studies(14, 19) have shown that segmental motion and diffusion of a penetrant in PIB may be correlated, which is not generally the case for other polymers. This was attributed to the very efficient molecular packing of the polymer(20-22). This high density of PIB relative to many other polymers implies that chain reorientation must accompany translational motion of the penetrant. The objective of this work is to compare the time scale of segmental motion of the polymer with the self - diffusion coefficient of the toluene in the PIB - toluene solutions as a function of concentration to see if they are indeed correlated. Segmental motion in pure PIB has been examined in detail in a recent report(14) and that information will serve as a guide in the interpretation of the concentration dependent results to be presented here.

The molecular tumbling of liquid toluene has been studied(23-24) earlier via spin - lattice relaxation time measurements and it has been found that the relaxation time of the ortho ^{13}C is dominated by the intramolecular dipole - dipole interaction with the attached proton. Because of the r^{-6} dependence of the dipole - dipole interaction, intermolecular interactions for carbons directly bound to a hydrogen atom(24) can be neglected. Other mechanisms, such as spin rotation and chemical shift anisotropy, have little contribution to the spin - lattice relaxation time. It is secondary goal to examine toluene in the PIB - toluene system and see if it behaves in a similar way to the pure liquid state and try to obtain additional information about the solution free volume.

A comparison of the time scale of reorientational motion of the solvent with the segmental motion of the polymer is required to determine the applicability of the Kramers relationship(25) in dilute solution. Zhu et al.(26) have shown that this relation fails when the rotational motion of the solvent is comparable or slower than the time scale of segmental motion.

Experimental

The polyisobutylene sample used for the study was obtained from Cellomer Associates, Inc. of Webster, NY in the form of thick sheets of high molecular weight (Cat. #40E, Lot #02, mol. wt. 1,000,000). HPLC Grade toluene was obtained from FisherChemical Fisher Scientific. NMR experiments were carried out on a Bruker AC-200, MSL-300 and Varian Unity 500 spectrometers, which correspond to 50.33 MHz, 75.5 MHz and 125.7 MHz ^{13}C Larmor frequencies respectively. The measurements of the spin - lattice relaxation time for the ortho carbon of toluene were performed on the AC-200 and the MSL-300.

A simple 180° - τ - 90° pulse sequence was used for the spin - lattice relaxation time measurements. Two to three hours have been allowed for the sample to reach thermal equilibrium before each measurement.

Results

Spin -lattice relaxation times for the methylene carbon of PIB and the ortho phenyl carbon of toluene are presented in Figures 1-8 as a function of concentration and temperature.

Interpretation

The equations that relate the spectral density function and the spin - lattice relaxation time are given by:

$$\frac{1}{T_1} = W_0 + 2W_{1C} + W_2 \qquad (1)$$

where

$$W_0 = \sum_j \gamma_C^2 \gamma_H^2 \hbar^2 \frac{J_0(\omega_H - \omega_C)}{20 r_j^6} \qquad (2)$$

$$W_{1C} = \sum_j 3\gamma_C^2 \gamma_H^2 \hbar^2 \frac{J_1(\omega_C)}{40 r_j^6} \qquad (3)$$

$$W_2 = \sum_j 3\gamma_C^2 \gamma_H^2 \hbar^2 \frac{J_2(\omega_H + \omega_C)}{10 r_j^6} \qquad (4)$$

The methylene C - H distance is set at 1.09 Å.

The spectral density function that was used to interpret the T_1 data, is the Hall - Helfand function(15) combined with restricted anisotropic rotational diffusion(14, 27-30). The spectral density function is shown below:

$$J(\omega) = \{A + \frac{B}{\ell^2}[(1-\cos\ell)^2 + \sin^2\ell] + \frac{C}{4\ell^2}[(1-\cos 2\ell)^2 + \sin^2 2\ell]\} J^{01}(\omega) +$$

$$+\frac{B}{2}\sum_{n=1}^{\infty}[(\frac{1-\cos(\ell-n\pi)}{\ell-n\pi} + \frac{1-\cos(\ell+n\pi)}{\ell+n\pi})^2 + (\frac{\sin(\ell-n\pi)}{\ell-n\pi} + \frac{\sin(\ell+n\pi)}{\ell+n\pi})^2 J^{\lambda_n}(\omega) +$$

$$+\frac{C}{2}\sum_{n=1}^{\infty}[(\frac{1-\cos(2\ell-n\pi)}{2\ell-n\pi} + \frac{1-\cos(2\ell+n\pi)}{2\ell+n\pi})^2 + (\frac{\sin(2\ell-n\pi)}{2\ell-n\pi} + \frac{\sin(2\ell+n\pi)}{2\ell+n\pi})^2 J^{\lambda_n}(\omega)$$

where

$$J^{01}(\omega) = 2\{[\tau_0^{-1}(\tau_{01}^{-1} + \tau_1^{-1}) - \omega^2]^2 + [2\tau_{01}^{-1}\omega]^2\}^{-1/4} \cos[\frac{1}{2}\tan^{-1}\frac{2\tau_{01}^{-1}\omega}{\tau_0^{-1}(\tau_{01}^{-1} + \tau_1^{-1}) - \omega^2}]$$

$$J^{\lambda_n}(\omega) = 2\{[(\tau_0^{-1} + \lambda_n)(\tau_{01}^{-1} + \tau_1^{-1} + \lambda_n) - \omega^2]^2 + [2(\tau_{01}^{-1} + \lambda_n)\omega]^2\}^{-1/4}$$

$$\otimes \cos[\frac{1}{2}\tan^{-1}\frac{2(\tau_{01}^{-1} + \lambda_n)\omega}{(\tau_0^{-1} + \lambda_n)(\tau_{01}^{-1} + \tau_1^{-1} + \lambda_n) - \omega^2}]$$

where

$$\tau_{01}^{-1} = \tau_0^{-1} + \tau_1^{-1} ; \qquad \lambda_n = (\frac{n\pi}{\ell})^2 D_{ir} \qquad (5)$$

and

$$A = \frac{1}{4}(3\cos^2\Delta - 1)^2; \qquad B = \frac{3}{4}(\sin^2 2\Delta); \qquad C = \frac{3}{4}(\sin^4\Delta) \qquad (6)$$

The angle Δ is between the internuclear vector and the axis of rotation, the latter being the carbon - carbon backbone bonds for this case.

According to this model two correlation times describe the segmental motion of the polymer. One of them is τ_0 which is the correlation time for single conformational transitions and the other is τ_1 the correlation time for cooperative or correlated transitions. Each of these two correlation times was given an Arrhenius temperature dependence with activation energy E_{a0} and E_{a1} respectively. Also ℓ is the amplitude over which restricted rotational diffusion occurs and D_{ir} is the rotational diffusion constant. The form of the temperature dependence of ℓ and D_{ir} is shown below:

$$\ell = A\,T^{0.5}\ \text{deg} \qquad (7)$$

$$D_{ir} = B\,T - C\ \text{sec}^{-1} \qquad (8)$$

When the Arrhenius temperature dependence was used, seven parameters are required, namely: $(\tau_\infty)_0$, $(\tau_\infty)_1$, E_{a0}, E_{a1}, A, B, C and:

$$\tau_0 = (\tau_\infty)_0 \exp(E_{a0} / R\,T) \qquad (9)$$

$$\tau_1 = (\tau_\infty)_1 \exp(E_{a1} / R\,T) \qquad (10)$$

However, it is not necessary to float all seven parameters to fit the experimental data as several are essentially predetermined. A previous study of PIB(13) in solution showed that the libration does not change from the bulk state to solution. Therefore the parameters ℓ and D_{ir} were kept constant and equal to the values obtained from the study(14) of neat PIB. Also during the fitting process the $(\tau_\infty)_0$ and $(\tau_\infty)_1$, did not seem to change much and thus they were kept constant and equal to the values obtained from the study(14) of neat PIB. Therefore only two parameters (E_{a0} and E_{a1}) were left to float in order to fit the spin - lattice relaxation data of the methylene carbon of PIB in toluene - PIB solutions as a function of temperature and concentration. The results are shown in Table 1 while the rest of the parameters have the values:

$$(\tau_\infty)_0 = 2.1\ 10^{-14}\ \text{sec};\quad (\tau_\infty)_1 = 1.0\ 10^{-14}\ \text{sec} \qquad (11)$$

$$\ell = 5.15\ T^{0.5}\ \text{deg};\qquad D_{ir} = 3.26\ 10^{7}\ T - 3.5\ 10^{9}\ \text{sec}^{-1} \qquad (12)$$

The curves associated with the fitting are compared with the data in Figures 1 - 6.

When a WLF temperature dependence was given to the correlation times, there are six parameters to be established: $(\tau_0)_0$, $(\tau_1)_0$, ℓ, D_{ir}, $c_1{}^0$ and $c_2{}^0$ ($c_1{}^0$ and $c_2{}^0$ are the WLF coefficients). The reference temperature was chosen to be $T_0 = 298$ K and accordingly:

$$\ln\frac{\tau_0}{(\tau_0)_0} = \frac{-2.303c_1^0(T-T_0)}{c_2^0+T-T_0} \qquad (13)$$

$$\ln\frac{\tau_1}{(\tau_1)_0} = \frac{-2.303c_1^0(T-T_0)}{c_2^0+T-T_0} \qquad (14)$$

$$c_1^0 = \frac{B_0}{2.303f(\phi_s)} \qquad (15)$$

$$c_2^0 = \frac{f(\phi_s)}{\alpha} \qquad (16)$$

where $f(\phi_s)$ is the fractional free volume of the solution and α is the thermal expansion coefficient of the fractional free volume. B_0 represents the minimum void size necessary for a conformational transition.

Again ℓ and D_{ir} were kept constant and equal to the values obtained for the neat PIB(14) corresponding to the WLF temperature dependence:

$$\ell = 5.4\ T^{0.5}\ \text{deg and } D_{ir} = 2.1\ 10^{7}\ T\ \text{sec}^{-1}$$

Also $c_2{}^0$ was set equal to $c_2{}^D$ the WLF coefficient obtained from the study(17) of the temperature dependence of the self - diffusion coefficient of toluene in PIB - toluene solutions. The parameters that were floated to fit the data are $(\tau_0)_0$, $(\tau_1)_0$ and $c_1{}^0$. The values obtained are shown in Table 2. Comparable fittings to those shown in Figures 1 - 6 were obtained from the analysis of the T_1 data when a WLF temperature dependence was given to the correlation times.

From the WLF coefficients $c_1{}^0$ shown in Table 2 and equation (15) we can extract values for the fractional free volume of the solution. The results are shown in Table 3, where the fractional free volume of the solution (for different concentrations) obtained from the T_1 data is compared with the corresponding values obtained from the self - diffusion coefficient data analysis(17). In both cases the reference temperature is 298 K. In Table 3, B_d represents the minimum void size necessary for a molecule to undergo a displacement. In general B_d is different from B_0 because they are associated with different modes of motion: B_d is associated with translational diffusion while B_0 is associated with conformational transitions.

As can be seen from Figures 7 and 8 there is no field strength dependence in the T_1 data for toluene. Therefore, the extreme narrowing limit equation is used for the interpretation of the T_1 data for the ortho carbon of toluene in PIB - toluene solution and is shown below :

$$\frac{1}{T_1} = \frac{4}{3}\gamma_H^2\gamma_C^2\hbar^2 S(S+1)\tau\frac{1}{r_{CH}^6} \tag{17}$$

where S = 1 / 2, τ is the correlation time for molecular tumbling and r_{CH} = 1.08 Å is the distance between the proton and the carbon on the toluene phenyl ring.

Again, at first an Arrhenius temperature dependence was given to the correlation time:

$$\tau = \tau_\infty \exp(E / R\,T) \tag{18}$$

where E is the activation energy for rotation and τ_∞ is a prefactor. Two parameters were floated E and τ_∞. During the fitting procedure it was found that τ_∞ is around 1.0×10^{-14} sec and changes little as a function of concentration. Thus the value of τ_∞ was set equal to $1.0\ 10^{-14}$ sec and E was the only parameter that was floated as concentration changed. The parameters obtained are shown in Table 4. The fitting curves are represented by the solid lines in Figures 7 and 8.

Next a WLF temperature dependence was assigned to the correlation time τ:

$$\ln\frac{\tau}{\tau_0} = \frac{-2.303c_1^0(T-T_0)}{c_2^0+T-T_0} \tag{19}$$

where τ_0 is the value of the correlation time τ at the reference temperature T_0 which again was chosen to be 298 K. $c_1{}^0$ and $c_2{}^0$ are the WLF coefficients at the reference temperature:

$$c_1^0 = \frac{B}{2.303 f(\phi_s)} \tag{20}$$

$$c_2^0 = \frac{f(\phi_s)}{\alpha} \tag{21}$$

where $f(\phi_s)$ is the fractional free volume of the solution and α is the thermal expansion coefficient of the fractional free volume of the solution. B represents the minimal void size necessary for rotation. For the fitting process of the T_1 data c_2^0 was set equal to c_2^D the WLF coefficient obtained from the temperature dependence of the self - diffusion of toluene in PIB - toluene solutions(17). The parameters that were floated in order to fit the data are c_1^0 and τ_0. the values obtained are shown in Table 5. The fittings obtained are comparable to those shown in Figures 7 and 8 for the Arrhenius temperature dependence.

Discussion

In this work three different kind of motions were considered: the self - diffusion of toluene in high molecular weight PIB, the molecular rotation of toluene and the segmental motion of the polymer. In general the c_1^0 WLF coefficient obtained from these three types of motion should be different, because of the different hole sizes required for each type of motion to occur, i.e., B's (in general $c_1^0 = B/2.303f(\phi_s)$ and $c_2^0 = f(\phi_s) / \alpha$). For the case of diffusion we have B_d, for the toluene rotation B and for the segmental motion of the polymer B_0.

In Table 3, $(f(\phi_s) / B_0)$ obtained from segmental motion and $(f(\phi_s) / B_d)$ obtained from translational diffusion are compared. From Table 3, it can be seen that the two parameters are close to each other, considering their uncertainties: of the order of ± 0.015 at low concentration, up to ± 0.05 at high toluene concentrations. The agreement is very good noting that the values are extracted from two completely different sets of data that describe different components of the solution. The toluene self - diffusion data were collected by observing directly the toluene molecule and the T_1 data were collected by observing the methylene carbon of PIB in the toluene - PIB solutions. The fractional free volume of the solution was extracted using two completely different methods that observe two different components of the solution. Therefore, from Table 3, since the fractional free volume of the solution, $f(\phi_s)$ and the thermal expansion coefficient of the free volume, α, are unique and independent of the type of motion that is examined, it can be concluded that $B_d \approx B_0$.

This conclusion is supported by a previous study(14) which showed that the segmental motion of PIB is correlated with the translational diffusion of CO_2. The fact that $B_d \approx B_0$ implies that the same relationship holds for the toluene - PIB system, when a toluene molecule is surrounded by polymer segments. Also the value of ξ, obtained from the Vrentas - Duda theory(18) is 0.892 which corresponds to a polymer jumping unit with molecular weight 94.3. This is very close to the molecular weight of toluene which is 92. The fact that the two nearly coincide with each other means that the two jumping units will need the same minimal free volume for translation (for toluene) and a conformational transition (for the polymer). This also indicates that B_d should equal B_0.

Another way to check to see if the two motions are correlated, is to directly compare the correlation time for translational diffusion τ_D and the correlation time for segmental motion (correlation time for single conformational transition). The first can be obtained from$^{(31)}$:

$$\tau_D = \frac{b^2}{D} \tag{22}$$

where D is the self - diffusion coefficient of toluene, b is the distance of closest approach which is between 2.2 Å - 3.3 Å. Using 2.7 Å as the distance of closest approach and the self - diffusion of toluene in PIB - toluene solution,$^{(17)}$ the correlation time for translational diffusion is calculated and shown in Table 6. The correlation time for a conformational transition, τ_0, is calculated from equations (9), (11) and Table 1. τ_0 is also shown in Table 6. Looking at Table 6 it can be seen that the two correlation times are close to each other at 0.045 toluene volume fraction which means at this low penetrant concentration the two motions (segmental and translational diffusion) are correlated. As we go to higher concentrations the difference between the τ_0 correlation time and the τ_D becomes larger up to two orders of magnitude at 0.712 toluene volume fraction (see Table 7). This might be expected since as we go towards higher concentrations a toluene molecule has fewer polymer molecules in its neighbourhood and it is not necessary for a polymer segment to move in order a toluene molecule to translate.

Thus we see that the two processes (diffusion and conformational transition) require similar minimum free volumes in order to occur. The diffusion of small molecules in PIB is affected by the free volume which in turn influences the molecular mobility of the polymer. Also the time scale of the two motions are correlated at low concentrations of penetrant.

The activation energies E_{a0} and E_{a1} as a function of the volume fraction of toluene in PIB are shown in Figure 9. The WLF coefficient $c_1{}^0$ obtained from T_1 data analysis and $c_1{}^D$ obtained from the self - diffusion data analysis are shown in Figure 10. The trends here are as expected and the agreement between the two WLF fittings is encouraging.

The spin - lattice relaxation data on the ortho carbon of toluene do not provide as much information about the motion of toluene as the corresponding data on PIB. However, at all concentrations the correlation time for toluene reorientation is two or more orders of magnitude faster than segmental motion and translational diffusion. Thus the reorientational motion of the toluene is uncoupled from the other two motions. The WLF analysis of the temperature dependence also leads to different values of $c_1{}^0$ and thus B further supporting the separation of these motions. A comparison of $f(\phi_s) / B_d$ with $f(\phi_s) / B$ is shown in Table 8. Toluene reorientation would appear to be a much more rapid motion involving a smaller hole size. The separation of the time scale of solvent reorientation from segmental motion at low PIB concentration also points to a likely Kramers dependence of segmental motion on solvent viscosity in dilute solutions though only a single solvent is considered in this study.

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Table 1

Activation energies for conformational transitions as a function of concentration of toluene in PIB.

Volume Fraction of toluene in PIB.	E_{a0} (kJ / mole)	E_{a1} (kJ / mole)
0.045	34.0	34.5
0.104	33.4	33.7
0.205	32.7	32.0
0.327	31.9	30.0
0.409	31.7	28.4
0.712	30.4	25.7

Table 2

Fitting parameters of the spin - lattice relaxation data when a WLF temperature dependence was given to the correlation times.

Volume Fraction of toluene in PIB	$(\tau_0)_0$ (sec)	$(\tau_1)_0$ (sec)	c_1^0	c_2^0 (K)
0.045	$3.00\ 10^{-8}$	$1.20\ 10^{-8}$	4.30	155.06
0.104	$1.80\ 10^{-8}$	$8.40\ 10^{-9}$	3.80	153.50
0.205	$8.85\ 10^{-9}$	$4.25\ 10^{-9}$	3.40	175.17
0.327	$6.23\ 10^{-9}$	$1.88\ 10^{-9}$	2.75	183.65
0.409	$3.40\ 10^{-9}$	$9.70\ 10^{-10}$	2.65	197.92
0.712	$3.00\ 10^{-9}$	$4.00\ 10^{-10}$	1.85	245.45

Table 3

Fractional free volume comparison of the PIB - toluene solutions obtained from the diffusion data analysis(17) and from the T_1 data presented in this work.

Volume fraction of toluene in PIB ϕ_s	$f(\phi_s) / B_d$ From Diffusion data	$f(\phi_s) / B_0$ From T_1 data
0.045	0.090	0.101
0.104	0.105	0.114
0.205	0.127	0.127
0.327	0.155	0.158
0.409	0.190	0.164
0.712	0.270	0.235

Table 4

Fitting parameters of the ortho carbon T_1 data when an Arrhenius temperature dependence was given to the correlation time.

Volume fraction of toluene in PIB ϕ_s	τ_∞ (sec)	E (kJ / mole)
0.045	$1.0\ 10^{-14}$	22.73
0.104	$1.0\ 10^{-14}$	21.84
0.205	$1.0\ 10^{-14}$	20.76
0.327	$1.0\ 10^{-14}$	18.50
0.409	$1.0\ 10^{-14}$	16.77
0.712	$1.0\ 10^{-14}$	14.00

Table 5

Fitting parameters of the ortho carbon T_1 data when a WLF temperature dependence was given to the correlation time.

Volume fraction of toluene in PIB ϕ_S	τ_0 (sec) at T_0 298K	c_1^0 at 298 K	c_2^0 (K) at 298 K
0.045	$9.72\ 10^{-11}$	2.45	155.06
0.104	$6.80\ 10^{-11}$	2.35	153.50
0.205	$4.10\ 10^{-11}$	2.25	175.17
0.327	$1.67\ 10^{-11}$	2.10	183.65
0.409	$8.40\ 10^{-12}$	2.00	197.92
0.712	$2.90\ 10^{-12}$	1.81	245.45

Table 6

Comparison of the correlation times for diffusion, τ_D, and for single conformational transitions τ_0 for 0.045 toluene volume fraction.

D (cm^2 / sec) Toluene Volume Fraction = 0.045	T (K)	τ_0 (sec)	τ_D (sec)
$2.55\ 10^{-8}$	298	$1.915\ 10^{-8}$	$2.859\ 10^{-8}$
$6.66\ 10^{-8}$	310	$1.126\ 10^{-8}$	$1.095\ 10^{-8}$
$1.26\ 10^{-7}$	320	$7.453\ 10^{-9}$	$5.786\ 10^{-9}$
$2.04\ 10^{-7}$	329	$5.254\ 10^{-9}$	$3.574\ 10^{-9}$
$3.11\ 10^{-7}$	339	$3.642\ 10^{-9}$	$2.344\ 10^{-9}$
$4.55\ 10^{-7}$	348	$2.666\ 10^{-9}$	$1.602\ 10^{-9}$
$6.31\ 10^{-7}$	357	$1.982\ 10^{-9}$	$1.155\ 10^{-9}$
$8.14\ 10^{-7}$	367	$1.451\ 10^{-9}$	$8.956\ 10^{-10}$

Table 7

Comparison of the correlation times for diffusion, τ_D, and for single conformational transitions τ_0 for 0.712 toluene volume fraction.

D (cm^2 / sec) Toluene Volume Fraction = 0.712	T (K)	τ_0 (sec)	τ_D (sec)
$3.1\ 10^{-6}$	249	$5.008\ 10^{-8}$	$2.352\ 10^{-10}$
$4.02\ 10^{-6}$	259	$2.841\ 10^{-8}$	$1.813\ 10^{-10}$
$5.09\ 10^{-6}$	269	$1.681\ 10^{-8}$	$1.432\ 10^{-10}$
$5.79\ 10^{-6}$	280	$9.854\ 10^{-9}$	$1.259\ 10^{-10}$
$8.00\ 10^{-6}$	298	$4.478\ 10^{-9}$	$9.113\ 10^{-11}$
$9.90\ 10^{-6}$	310	$2.785\ 10^{-9}$	$7.364\ 10^{-11}$
$1.19\ 10^{-5}$	320	$1.926\ 10^{-9}$	$6.339\ 10^{-11}$
$1.41\ 10^{-5}$	329	$1.409\ 10^{-9}$	$5.170\ 10^{-11}$
$1.46\ 10^{-5}$	339	$1.015\ 10^{-9}$	$4.993\ 10^{-11}$
$1.81\ 10^{-5}$	348	$7.681\ 10^{-10}$	$4.028\ 10^{-11}$
$1.94\ 10^{-5}$	357	$5.893\ 10^{-10}$	$3.758\ 10^{-11}$

Table 8

Fractional free volume comparison of the PIB - toluene solutions obtained from the diffusion data analysis(17) and from the T_1 data of the ortho carbon - 13 of toluene presented in this work.

Volume fraction of toluene in PIB ϕ_S	$f(\phi_S) / B_d$ From Diffusion data	$f(\phi_S) / B$ From T_1 data
0.045	0.090	0.177
0.104	0.105	0.185
0.205	0.127	0.193
0.327	0.155	0.207
0.409	0.190	0.217
0.712	0.270	0.240

Figure Captions

Figure 1: T_1 of the methylene carbon of PIB in toluene - PIB solutions as a function of temperature and Larmor frequency. The volume fraction of toluene in PIB is 0.045. An Arrhenius temperature dependence was given to the correlation times. The solid line corresponds to the fit for the Hall - Helfand function combined with anisotropic restricted rotational diffusion.

Figure 2: T_1 of the methylene carbon of PIB in toluene - PIB solutions as a function of temperature and Larmor frequency. The volume fraction of toluene in PIB is 0.104. An Arrhenius temperature dependence was given to the correlation times. The solid line corresponds to the fit for the Hall - Helfand function combined with anisotropic restricted rotational diffusion.

Figure 3: T_1 of the methylene carbon of PIB in toluene - PIB solutions as a function of temperature and Larmor frequency. The volume fraction of toluene in PIB is 0.205.

An Arrhenius temperature dependence was given to the correlation times. The solid line corresponds to the fit for the Hall - Helfand function combined with anisotropic restricted rotational diffusion.

Figure 4: T_1 of the methylene carbon of PIB in toluene - PIB solutions as a function of temperature and Larmor frequency. The volume fraction of toluene in PIB is 0.327. An Arrhenius temperature dependence was given to the correlation times. The solid line corresponds to the fit for the Hall - Helfand function combined with anisotropic restricted rotational diffusion.

Figure 5: T_1 of the methylene carbon of PIB in toluene - PIB solutions as a function of temperature and Larmor frequency. The volume fraction of toluene in PIB is 0.409. An Arrhenius temperature dependence was given to the correlation times. The solid line corresponds to the fit for the Hall - Helfand function combined with anisotropic restricted rotational diffusion.

Figure 6: T_1 of the methylene carbon of PIB in toluene - PIB solutions as a function of temperature and Larmor frequency. The volume fraction of toluene in PIB is 0.712. An Arrhenius temperature dependence was given to the correlation times. The solid line corresponds to the fit for the Hall - Helfand function combined with anisotropic restricted rotational diffusion.

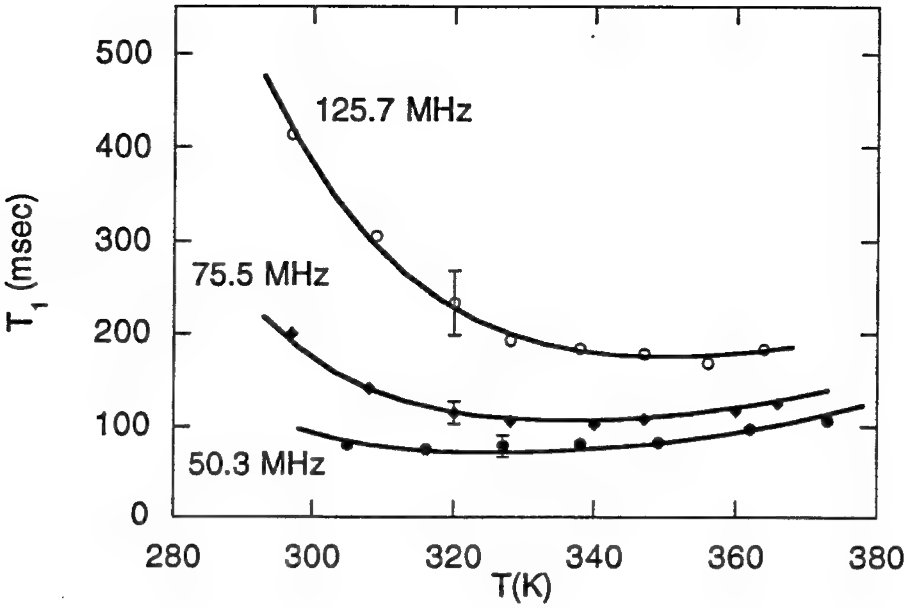
Figure 7: T_1 of the ortho ^{13}C of toluene in PIB - toluene solutions as a function of temperature concentration and Larmor frequency. The numbers shown next to the curves represent the volume fraction of toluene in the solution. An Arrhenius temperature dependence was given to the correlation time τ. The solid lines correspond to the T_1 values calculated from equation 17.

Figure 8: T_1 of the ortho ^{13}C of toluene in PIB - toluene solutions as a function of temperature concentration and Larmor frequency. The numbers shown next to the curves represent the volume fraction of toluene in the solution. An Arrhenius temperature dependence was given to the correlation time τ. The solid lines correspond to the T_1 values calculated from equation 17.

Figure 9: Activation energies as a function of concentration obtained from the Arrhenius temperature dependence of the correlation times.

Figure 10: WLF coefficients as a function of concentration.

fig 1


500
400
300
200
100
0
T_1 (msec)
280
300
320
340
360
380
T(K)
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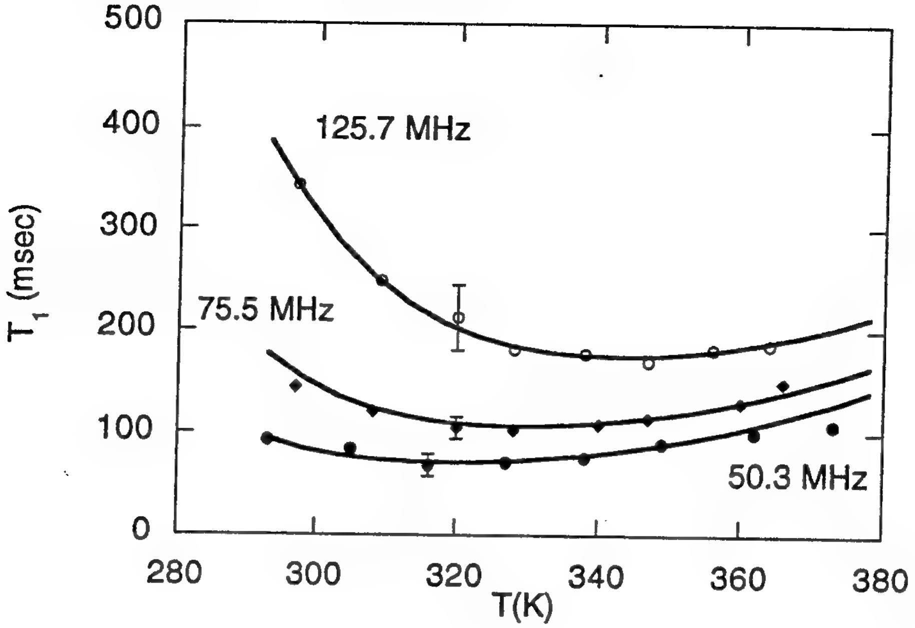
75.5 MHz
50.3 MHz

fig 2



125.7 MHz
75.5 MHz
50.3 MHz
T_1 (msec)
T(K)
0
100
200
300
400
500
280
300
320
340
360
380

fig 3

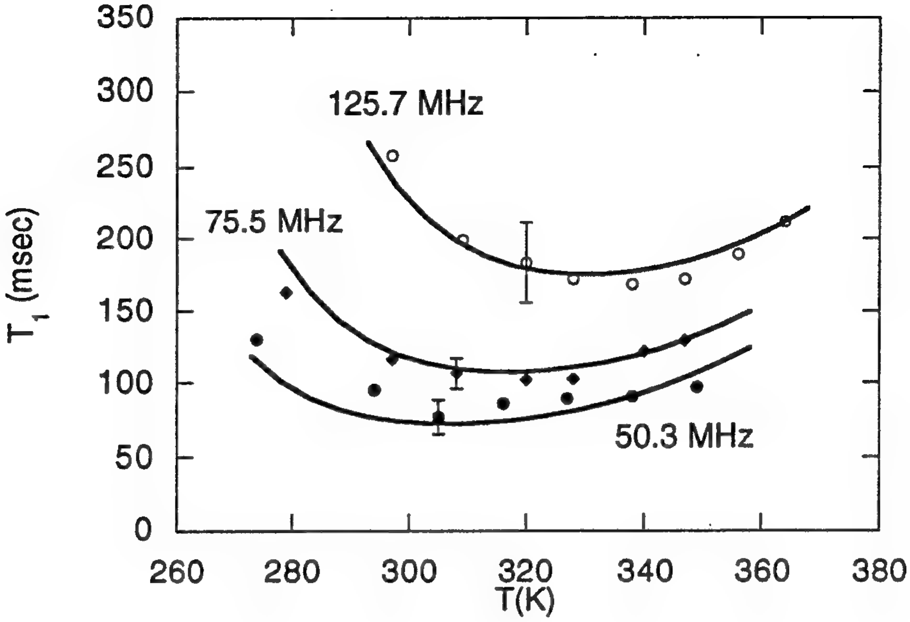

T$_1$ (msec)
T(K)
125.7 MHz
75.5 MHz
50.3 MHz
0
50
100
150
200
250
300
350
260
280
300
320
340
360
380

fig 4

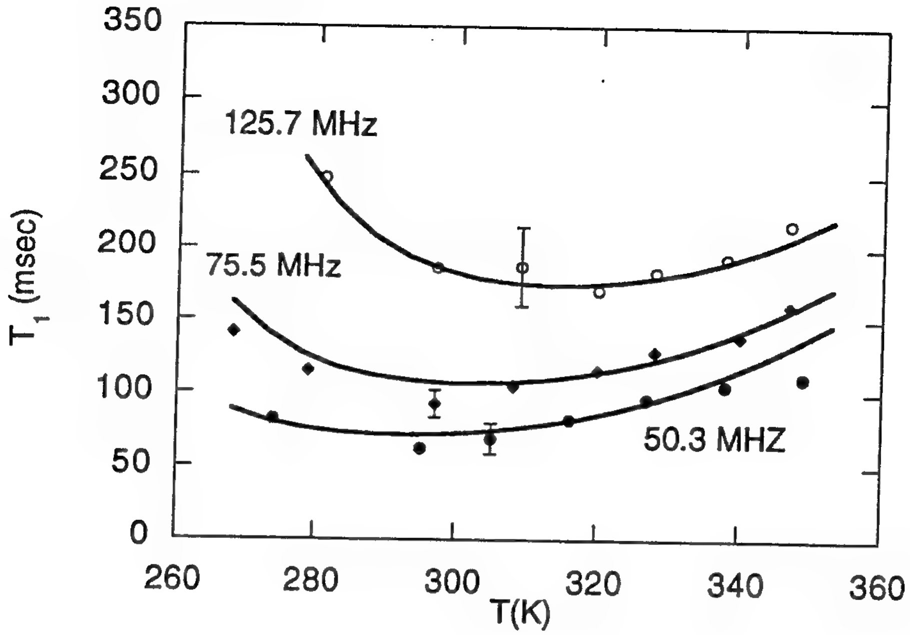

350
300
250
200
150
100
50
0
T₁ (msec)
125.7 MHz
75.5 MHz
50.3 MHZ
260
280
300
320
340
360
T(K)

fig 5

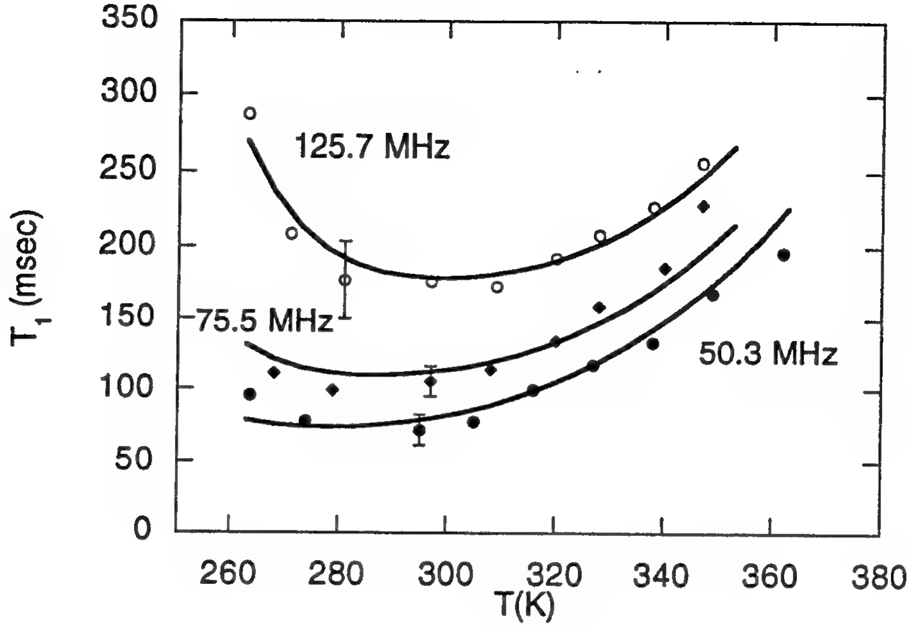

T₁ (msec)
350
300
250
200
150
100
50
0
260
280
300
320
340
360
380
T(K)
125.7 MHz
75.5 MHz
50.3 MHz

fig 6

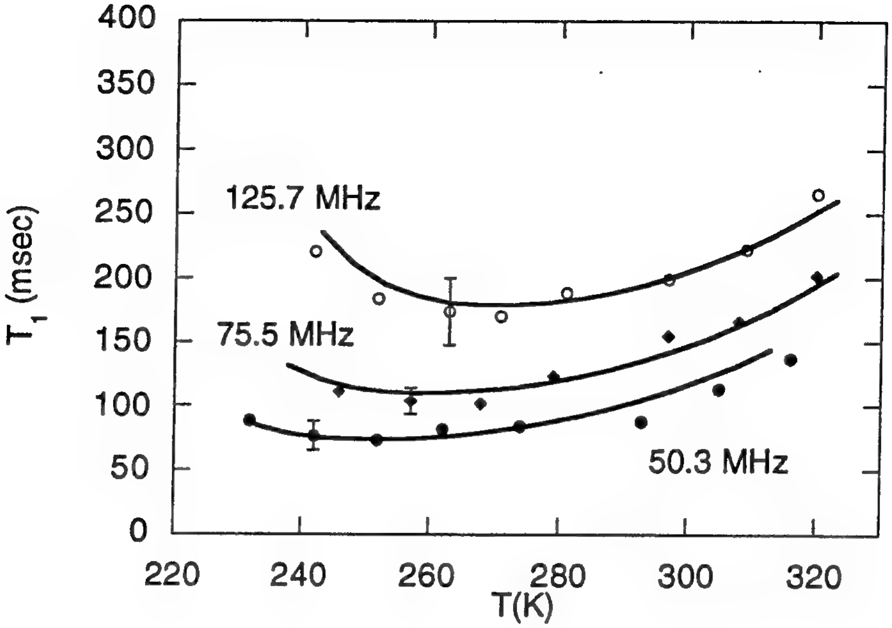

400
350
300
250
200
150
100
50
0
220
240
260
280
300
320
T(K)
T_1 (msec)
125.7 MHz
75.5 MHz
50.3 MHz

fig 7

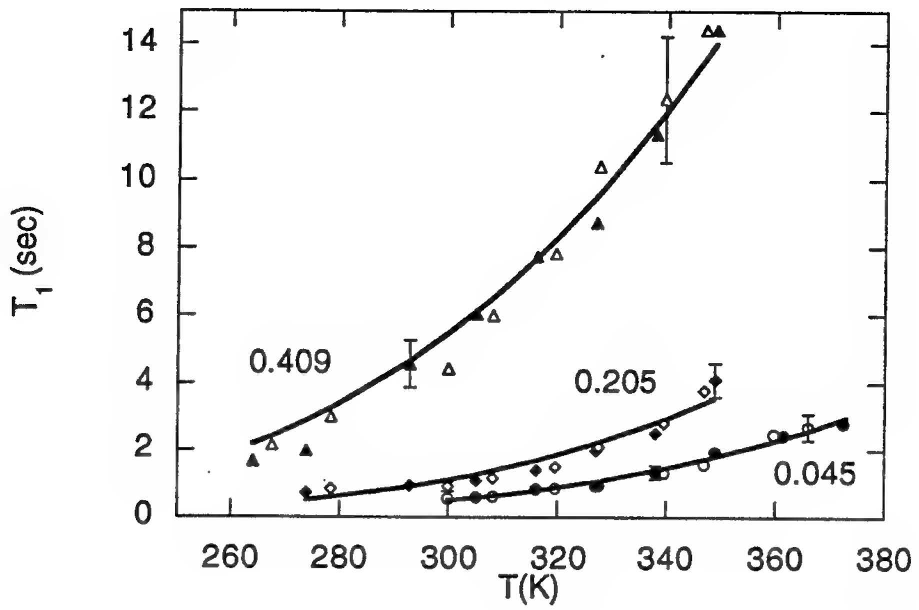

14
12
10
8
6
4
2
0
T$_1$ (sec)
260
280
300
320
340
360
380
T(K)
0.409
0.205
0.045

fig 8

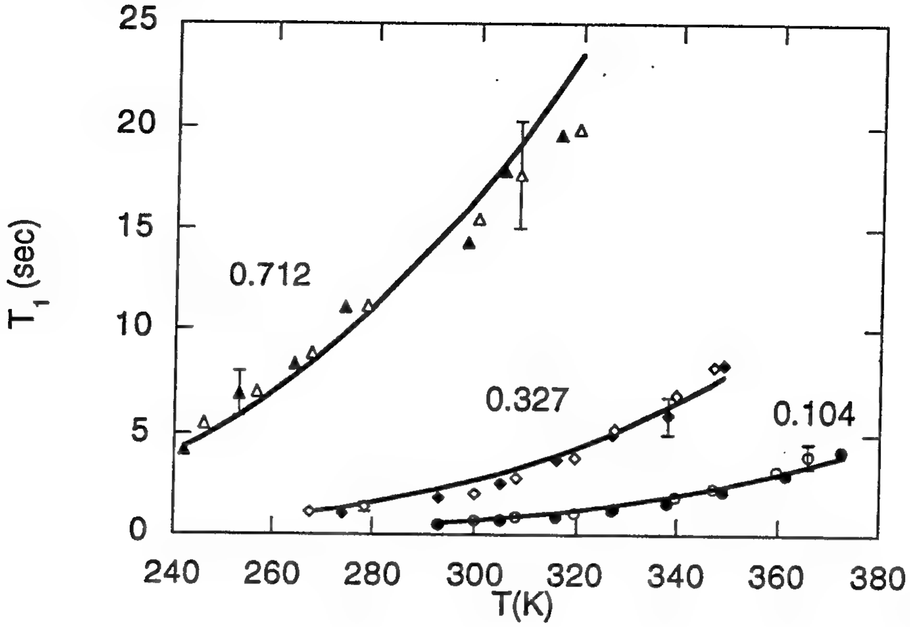
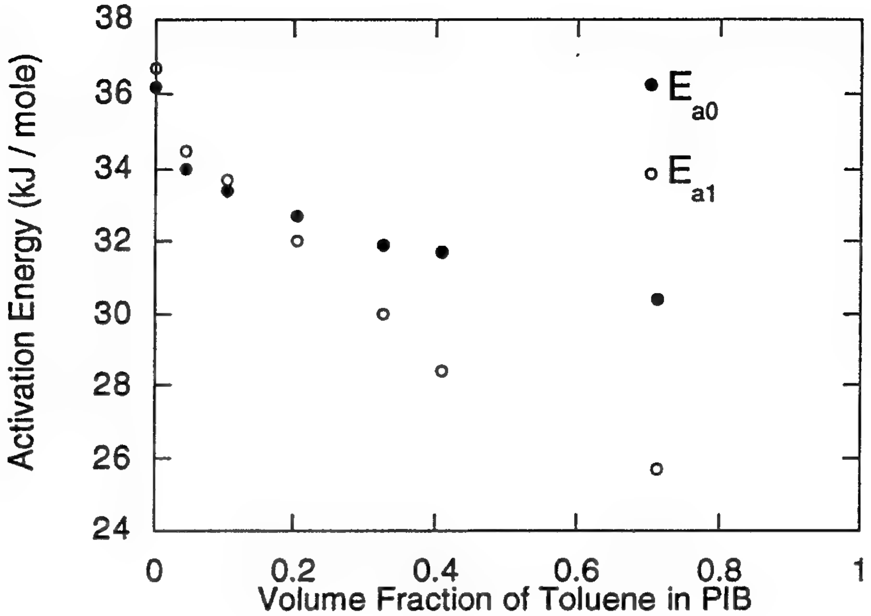
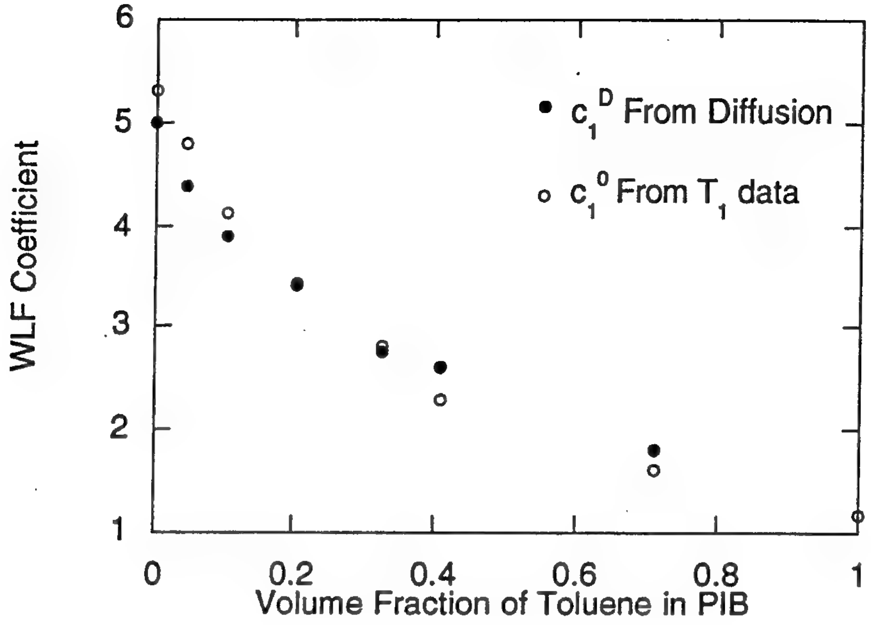

T₁ (sec)
25
20
15
10
5
0
240
260
280
300
320
340
360
380
T(K)
0.712
0.327
0.104

fig 9



38
36
34
32
30
28
26
24
Activation Energy (kJ / mole)
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene in PIB
● E_{a0}
○ E_{a1}

fig 10


WLF Coefficient
6
5
4
3
2
1
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene in PIB
● c_1^D From Diffusion
○ c_1^0 From T_1 data

A NMR Study of Penetrant Diffusion and Polymer Segmental Dynamics in Rubber.

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Introduction

Diffusion theories(1-3) utilizing free volume concepts are known to accurately model transport in both rubbery(4) and glassy polymers(5). A number of studies have been made concerning diffusion in polyisobutylene (PIB)(6-9). PIB is a special polymer because of its low permeability to gases and liquids. The low permeability may come from the fact that PIB has a low specific volume(10-12). Previous studies have shown that segmental motion and diffusion in PIB are correlated(13-14) while this is not generally the case for other polymers. In the present work the pulsed field gradient(PFG) NMR technique was used to directly measure the self-diffusion coefficient of toluene in PIB as a function of concentration and temperature. The ^{13}C spin-lattice relaxation time(T_1) of the methylene carbon of PIB was also determined to simultaneously monitor the segmental motion of the polymer in PIB/Toluene solutions.

Experimental

The NMR measurements were made on a Bruker MSL300 spectrometer. In the PFG technique an applied magnetic field gradient was varied from 14 gauss/cm up to 140 gauss/cm. The T_1's of the methylene carbon of PIB were determined from about 5wt % up to 70wt % of toluene in PIB.

Results and Interpretation

In figure 1 the self diffusion coefficient of toluene in PIB is shown as a function of temperature and concentration. In figure 2 the ^{13}C T_1's of the backbone methylene of PIB are shown as a function of temperature and Larmor frequency for 70wt % toluene in PIB.

The temperature dependence of the self-diffusion coefficients of toluene in PIB were fitted using the familiar WLF equation(15):

$$\ln\left(\frac{DT_0}{D_0T}\right)=\frac{\frac{\alpha(\phi_s)}{B_d}(T-T_0)}{\frac{f(\phi_s)}{B_d}\left(\frac{f(\phi_s)}{B_d}+\frac{\alpha(\phi_s)}{B_d}(T-T_0)\right)}$$

where ϕ_s is the volume fraction of toluene in PIB, $f(\phi_s)$ is the fractional free volume of the solution at the reference temperature T_0, $\alpha(\phi_s)$ is the fractional free volume expansion factor and B_d is a constant which corresponds to the minimum hole required for a given molecule to diffuse.

The parameters $f(\phi_s)/B_d$ and $\alpha(\phi_s)/B_d$ obtained from data fitting are:

ϕ_s	$f(\phi_s)/B_d$	$\alpha(\phi_s)/B_d$ (deg-1)	c_1^D	c_2^D
0	0.0818	5.34 10^{-4}	5.308	153.18
0.045	0.0904	5.83 10^{-4}	4.803	155.06
0.104	0.105	6.84 10^{-4}	4.135	153.51
0.205	0.127	7.25 10^{-4}	3.419	175.17
0.327	0.155	8.44 10^{-4}	2.801	183.65
0.409	0.190	9.60 10^{-4}	2.285	197.92
0.712	0.270	1.10 10^{-3}	1.608	245.45
1.000	0.396	1.70 10^{-3}	1.097	232.94

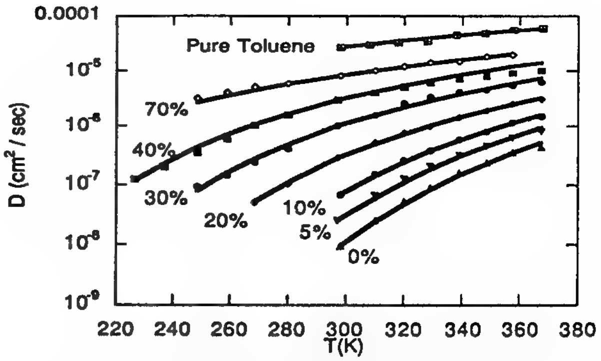

Fig. 1. Temperature Dependence of the toluene self - diffusion coefficient in PIB. The solid lines represent fittings from the WLF equation presented in the text.

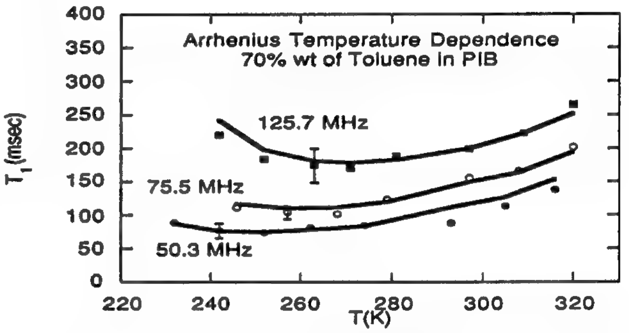

Fig. 2. Spin - Lattice relaxation times of the methylene carbon of PIB as a function of temperature and Larmor frequency. The concentration of toluene is about 70% wt. The solid lines represent fitting from the Hall-Helfand model combined with a restricted anisotropic rotational diffusion. An Arrhenius temperature dependence was given to the correlation times.

The data were also fit as a function of concentration at a constant temperature using the Fujita theory(1):

$$\ln\frac{D}{D_0}=\frac{B_d(f_s-f_p)\phi_s}{f_p^2+(f_s-f_p)f_p\phi_s}=\frac{\left[\left(\frac{f_s}{B_d}\right)-\left(\frac{f_p}{B_d}\right)\right]\phi_s}{\left(\frac{f_p}{B_d}\right)^2+\left[\left(\frac{f_s}{B_d}\right)-\left(\frac{f_p}{B_d}\right)\right]\left(\frac{f_p}{B_d}\right)\phi_s}$$

where the parameters are the same as above except that f_p is the average fractional free volume of pure polymer, f_s is the fractional free volume of toluene in the solution at the limit of zero toluene concentration(16) and D_0 is the diffusion coefficient of toluene at the limit of zero penetrant(toluene) concentration. The parameters varied are D_0, (f_p/B_d) and (f_s/B_d). The values for the parameters are:

T (K)	(f_s / B_d)	(f_p / B_d)	D_0 (cm² / sec)
298	0.273	0.08735	9.08 10^{-9}
310	0.300	0.0978	2.55 10^{-8}
320	0.333	0.1070	5.15 10^{-8}
329	0.364	0.1163	8.70 10^{-8}
339	0.381	0.1250	1.55 10^{-7}
349	0.398	0.1320	2.30 10^{-7}
358	0.423	0.1410	3.40 10^{-7}
368	0.449	0.1445	4.10 10^{-7}

The data were also fitted using the Vrentas - Duda theory(3):

$$D_1 = D_0 \exp(\frac{-E}{RT}) \exp[\frac{-(\omega_1 V_1^* + \omega_2 \xi V_2^*)}{\omega_1(\frac{K_{11}}{\gamma})(K_{21} - T_{g1} + T) + \omega_2(\frac{K_{12}}{\gamma})(K_{22} - T_{g2} + T)}$$

Where D_1 is the self diffusion coefficient of the penetrant and the other parameters are defined elsewhere(17). The values of the parameters are given in reference 17 except the values of K_{12}/γ and K_{22} - T_{g2} that were obtained from an NMR study of neat PIB(13); their values are 4.351 10^{-4} cm^3/gr K and -97.6 K respectively. The only parameter that was floated is ξ which is the ratio of molar volume of a solvent jumping unit over the molar volume of a polymer jumping unit:

$$\xi = \frac{V_1^0(0)}{V_{2j}} = \frac{M_1 V_1^*}{M_{2j} V_2^*}$$

where $V_1^0(0)$ is the solvent molar volume, V_{2j} is the jumping unit volume, M_1 is the molecular weight of the solvent and M_{2j} is the molecular weight of the polymer jumping unit and V_1^*, V_2^* are the specific critical hole free volumes of pure toluene and PIB respectively. The value of ξ is about 0.892 ± 0.08 which corresponds to a polymer jumping unit of molecular weight 94.3. A fitting of the diffusion coefficient as a function of concentration at two different temperatures for the two different theories is shown in figure 3.

The T_1 data of the methylene carbon of PIB in the toluene solutions were fitted using the Hall - Helfand model combined with libration13). The data were fitted using both a WLF approach with values obtained from the diffusion data and an Arrhenius temperature dependence for the correlation times.

One of the fittings is shown in figure 2. The parameters obtained for the Arrhenius temperature dependence show that the activation energies for the Hall-Helfand processes are close and decrease slightly with increasing toluene content with values from 34 to 26KJ/mole. Parameters that were constant at all concentrations are:

$\tau_0 = (\tau_\infty)_0 \exp(E_{a0}/RT)$, $\tau_1 = (\tau_\infty)_1 \exp(E_{a1}/RT)$, $\ell = A\ T^{0.5}$, $D_{ir} = B\ T - C$

$(\tau_\infty)_0 = 2.1\ 10^{-14}$ sec, $(\tau_\infty)_1 = 1.0\ 10^{-14}$ sec, $\ell = 5.15\ T^{0.5}$ deg, $D_{ir} = 3.26\ 10^{7}\ T - 3.5\ 10^{9}\ sec^{-1}$. Where τ_0 is the correlation time for single conformational transitions, τ_1 the correlation time for cooperative transitions, E_{a0}, E_{a1}, are the activation energies for τ_0 and τ_1 respectively, ℓ the angular amplitude over which rotational diffusion occurs and D_{ir} the rotational diffusion coefficient.

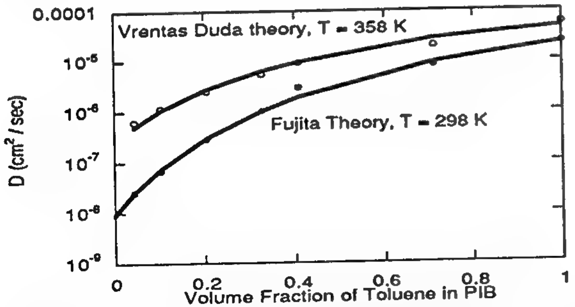

Fig.3 Fitting of the diffusion coefficient of toluene in PIB as a function of concentration at two temperatures using Fujita and Vrentas - Duda theory.

Discussion

It is clear from the above analysis that the self-diffusion of toluene in PIB is well described by free volume theories.In this work two types of motion are investigated: self-diffusion of toluene in high molecular weight PIB and segmental motion of the polymer. In general the c_1^0 WLF coefficient obtained from these two types of motion should be different, because of the different hole sizes, ie. B's (in general $c_1^0 = B/2.303f$ and $c_2^0 = f/\alpha$). For the case of diffusion we would have B_d, while for segmental motion, B. It seems from this study that B_d is equal to B since the diffusion and the T_1 data can be fitted using the same WLF coefficients, since f (fractional free volume of the solution) and α (thermal expansion coefficient of the fractional free volume) are unique and independent of the type of motion that is examined. This is supported by a previous study(13) that showed that the segmental motion of PIB is correlated with the translational diffusion of CO_2. The fact that B_d = B shows that the same thing happens for the toluene/PIB system. Also the value of ξ, obtained from the Vrentas - Duda theory is 0.892 which corresponds to a polymer jumping unit with molecular weight 94.3. This is very close to the molecular weight of toluene, which is 92. The fact that the two are very close to each other means that the two jumping units will need the same minimal free volume for translation (for toluene) and a conformational transition (for the polymer). This indicates that B_d = B. It seems that the diffusion of small foreign molecules in PIB is affected by the free volume which in turn influences the molecular mobility of the polymer.

Acknowledgement

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A NMR Study of Penetrant Diffusion and Polymer Segmental Motion in Toluene - Polyisobutylene Solutions.

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Abstract

The self - diffusion coefficients of toluene in polyisobutylene (PIB) solutions were determined using the Pulsed Field Gradient Nuclear Magnetic Resonance technique. The volume fraction of toluene in the polymer was varied from 0.045 up to 0.712 and the temperature was varied from 225 K up to 368 K. The concentration dependence of the data was interpreted using both the Fujita and the Ventras-Duda free volume theories and the temperature dependence was interpreted with the WLF equation. These models describe separately the concentration and temperature dependencies of the toluene self - diffusion coefficients very well and the resulting free volume parameters are in a good agreement with the ones extracted from the analysis of viscosity data on the same system. Comparisons were made between the two free volume theories and the Fujita free volume parameters could be extracted from the Vrentas - Duda free volume parameters.

The spin - lattice relaxation times are determined for the methylene carbon of polyisobutylene (PIB), as well as for the ortho carbon of toluene in toluene - polyisobutylene solutions. The Hall - Helfand correlation function combined with restricted anisotropic rotational diffusion was used to treat the T_1 data of the methylene carbon of PIB to characterize the polymer segmental motion. A simple exponential correlation function was used to describe the local motion of toluene in the solutions which falls in the extreme narrowing limit for the solutions studied. Both models described satisfactorily the temperature and field dependence of the spin - lattice relation times. From the temperature dependence of the correlation times for the polymer segmental motion, the free volume of the solution at each concentration is extracted and compared with the values obtained from the diffusion of the toluene penetrant. The free volume values extracted from the T_1 data for the methylene carbon of PIB and the self - diffusion data for the toluene were found to be in substantial agreement. The interrelationship of the timescale of segmental motion of the polymer and the translational diffusion of the toluene was also examined and it was found that the two types of motion seem to be correlated in high polymer concentration solutions. The toluene reorientational motion was found to be much faster than both the polymer segmental motion and the toluene translational diffusion leading to the conclusion that the toluene reorientational motion is uncoupled from these two motions.

Keywords: Polyisobutylene, Toluene, Pulse Field Gradient Nuclear Magnetic Resonance, Diffusion, Free Volume Theory, Segmental Motion.

Introduction

The diffusion of small molecules into polymers has been the subject of many investigations, because of its importance in industrial, medical and biological applications. Some examples are the membrane separation of gases, controlled drug delivery, control of polymerization, production of barrier materials for packaging and chemical defense. Diffusion of penetrants in polyisobutylene is of special interest since this material displays low permeability for a polymeric rubber well above the glass transition. This unusual property of polyisobutylene has been considered in computer simulations(1) of the rubber and in a detailed characterization of segmental motion(2) in the pure rubber by NMR.

There are a variety of techniques for measuring the self - diffusion coefficients of a penetrant in a polymer matrix. These include sorption, permeation, light scattering, radioactive tracing, forced Rayleigh scattering and Nuclear Magnetic Resonance (NMR). The Pulsed Field Gradient NMR Technique is valuable because it does not perturb the system. With this technique a direct measure of the self - diffusion coefficient of the penetrant is achieved by observing the molecules microscopically, while other methods (sorption method for example) indirectly determine the self - diffusion coefficient from macroscopic measurements. Also the experiment can give information about the geometry of the surroundings of the penetrant molecules in the case of heterogeneous systems; the dimension of the boundaries that the molecules may encounter and the mean square distance that the penetrant has travelled during the observation of diffusion. Other advantages of the technique are the ability to use small sample volumes, the precision of the measurements and the ability to be applied to both liquid and solid samples. The only limitation of the technique is that the lowest diffusion coefficient that can be commonly determined is around 10^{-9} cm^2 / sec to 10^{-10} cm^2 / sec.

In addition to the advantages of the Pulsed Gradient technique itself, with NMR the reorientational dynamics of the both the polymeric and penetrant components of the solution can be measured independently on the same sample. Thus both translational and rotational motion of the penetrant, and segmental motion of the polymer can be determined in the same samples. With modern NMR instrumentation, these measurements can be made over a wide range of temperatures and concentrations which lead to a fairly complete description of local dynamics. It is the goal of this work to present the results of such a complete set of NMR measurements on a single system beginning with translational diffusion of the penetrant.

Diffusion in polyisobutylene (PIB), has been studied before using different techniques(3 - 7). In references (3) and (4) the study of the diffusion coefficients of six hydrocarbons (propane, n - butane, isobutane, n - pentane, isopentane and neopentane) in PIB was reported using the sorption method. The self - diffusion of benzene in PIB has been studied in reference (5) using the pulsed field gradient technique over a limited range of temperatures and concentrations. In reference (6) the diffusion of radioactively tagged cetane in PIB has been studied and finally in reference (7) the diffusion of toluene in butyl rubber has been studied using the sorption method. In all cases the data were analyzed using the Fujita free volume theory. Viscosity data on polyisobutylene solutions are also available(8 - 11). In references (8 - 10) the intrinsic viscosities of PIB solutions in various solvents have been studied and their relations to polymer chain structure and to thermodynamic parameters governing the interaction between the polymer and the solvent have been made.

Free volume theories have been used widely for the interpretation of the concentration dependence of the self - diffusion of many small molecules into polymer matrices(12 - 15). One frequently used theory, developed almost thirty years ago(12), is the Fujita theory and a more recent free volume theory is that of Vrentas and Duda[13 - 15]. These two free volume theories differ in several respects and it will be of value to compare them in the context of a rather complete data set, not only including information of translational motion of the penetrant but also reorientational motion of both components: polymer and penetrant. The molecular level information available from NMR will provide insight into some of the concepts introduced into these theories which are at least at first glance based on very local descriptions of polymer and solvent dynamics.

The Fujita theory begins with the empirical result of Doolittle(16 - 17) who showed that the viscosity η of a liquid of low molecular weight is given by:

$$\ln\eta = \ln A + B / f \qquad (1)$$

where A and B are empirical constants for a given liquid and f is the fractional free volume, defined to be equal to the ratio of the volume of the space not occupied by the constituent molecules, v_f, over the total volume of the solution, v:

$$f = \frac{v_f}{v} \qquad (2)$$

$$v = v_0 + v_f \qquad (3)$$

where v_0 is the volume occupied by the molecules in accordance with Van der Waals radii and vibrational motions. Equation (1) measures the volume of a molecule relative to the volume of a void next to it. When the volume of the void is larger than the volume of the molecule the viscosity is low. When the volume of the void is smaller than the volume of the molecule the viscosity is high. Another assumption that is made is that the Doolittle relation applies to each jumping unit in polymer - solvent systems(18). Jumping units are imagined to be of the size of small penetrant molecules or repeat units in the case of the polymer. Also the theory relates the mobility of the polymer and the solvent jumping units to the free volume per unit volume of solution.

The Vrentas - Duda theory is based on the Cohen - Turnbull result(19) showing that the mobility of a molecule in a pure liquid is related to the average free volume, v_f, per molecule through the following equation:

$$\ln m = E - \gamma v^* / v_f \qquad (4)$$

where γ is a numerical factor between 0.5 and 1, also known as overlap factor, that is introduced because a given free volume may be available to more than one molecule and v^* is the minimum volume of a hole that a molecule must find in its vicinity in order for it to move. According to Cohen and Turnbull molecules are resident in cages bound by their neighbors for the majority of the time. When a density fluctuation occurs and a hole of enough size opens within the molecular cage, the molecule jumps into the hole. Diffusional motion is considered to be translation of a molecule across the space within its cage and bulk diffusion then occurs as a result of redistribution of the free volume within the liquid. The above equation was derived under the assumption that redistribution of free volume (holes) at constant volume requires no change in energy. Equation (4) demonstrates that when the minimum volume of a hole that a molecule must find for a jump to occur is larger than the average free volume per molecule then the mobility of the penetrant is small. Conversely, when v^* is smaller than v_f then the molecule can jump to a neighbouring position and the mobility is high.

Vrentas - Duda(13) formulated their theory based on the following assumptions as stated:

(i) V_f' is the free volume equal to the space not occupied by the actual molecules.

(ii) The free volume available to each jumping unit: solvent molecule or polymer segment, is equal to V_f' / N where N is the total number of solvent molecules plus polymer segments and V_f' is the total free volume of the solution.

(iii) The critical hole volume, v^*, of a jumping unit is equal to its intrinsic volume at zero Kelvin.

(iv) The partial specific volumes of the solvent and polymer are independent of composition i.e. there is no volume change on mixing and thermal expansion coefficients are given by their average values over the temperature range considered.

(v) As the temperature is increased, the increase in volume comes from the homogeneous expansion of the material due to the increasing amplitude of the anharmonic vibrations with temperature and from the formation of holes or vacancies which are distributed discontinuously throughout the material at any instant. The free space that is not occupied by the constituent molecules and is not associated with any holes or vacancies is called interstitial free volume. The energy for redistribution of the interstitial free volume is very large and this type of free volume therefore must be distributed uniformly among the molecules. The free volume associated with the discontinuous distribution of holes in the liquid is called the hole free volume. This free volume can be redistributed with no increase in energy.

In this study the temperature dependence will be analyzed using the WLF equation for diffusion(20), which is also commonly placed in the context of free volume theories. The well known form of the WLF equation is

$$\log_{10}\frac{\zeta}{\zeta_0} = \frac{-c_1^D(T-T_0)}{c_2^D+T-T_0} \qquad (5)$$

where ζ is the translational friction coefficient of a penetrant molecule into the polymer matrix, ζ_0 is the value of ζ at T_0 and $c_1{}^D$ and $c_2{}^D$ are the WLF coefficients at the reference temperature T_0. The diffusion coefficient ,D ,can be introduced into this equation by using the well known expression :

$$D = \frac{kT}{\zeta} \qquad (6)$$

where k is the Boltzmann's constant. The WLF equation can thus be applied to diffusion.

The local segmental motion of the polymer and the reorientational motion of the penetrant / solvent are determined using ^{13}C T_1 NMR measurements. Previous studies(2,21) have shown that segmental motion and diffusion of a penetrant in PIB may be correlated, which is not generally the case for other polymers. This was attributed to the very efficient molecular packing of the polymer(1). This high density of PIB relative to many other polymers implies that chain reorientation must accompany translational motion of the penetrant. The objective of this work is to compare the time scale of segmental motion of the polymer with the self - diffusion coefficient of the toluene in the PIB - toluene solutions as a function of concentration to see if they are indeed correlated. Segmental motion in pure PIB has been examined in detail in a recent report(2) and that information will serve as a guide in the interpretation of the concentration dependent results to be presented here.

Experimental

The polyisobutylene sample used for the study was obtained from Cellomer Associates, Inc. of Webster, NY in the form of thick sheets of high molecular weight (Cat. #40E, Lot #02, mol. wt 1,000,000). HPLC Grade toluene was obtained from FisherChemical Fisher Scientific. The diffusion measurements were performed on a Bruker MSL - 300 spectrometer equipped with a High Resolution Diffusion Unit and gradient probe, with a proton frequency of 300.1 MHz. For the diffusion measurements the phenyl proton peak of toluene was observed.

The well known Stejskal - Tanner pulse sequence(22) $\pi / 2 - G(\delta) - \pi - G(\delta)$ - (echo) was used to measure the diffusion coefficient of toluene in PIB solutions. The stimulated echo(23) pulse sequence $\pi / 2 - G(\delta) - \pi / 2 - \tau - \pi / 2 - G(\delta)$ - (echo) was also used for measuring the diffusion coefficient, employing longer diffusion time observations. The strength of the magnetic field gradients was varied from 14 gauss / cm up to 140 gauss / cm; the associated length δ, from 500 μsec up to 7 msec; and the distance between the two gradient pulses Δ, from 2 msec up to 80 msec. Those values of Δ correspond to diffusion distances from approximately 1.1 μm up to 9.1 μm.

NMR spin - lattice relaxation (T_1) experiments were carried out on Bruker AC-200, MSL-300 and Varian Unity 500 spectrometers, which correspond to 50.33 MHz, 75.5 MHz and 125.7 MHz ^{13}C Larmor frequencies respectively.

Interpretation

The temperature dependence of toluene in PIB was analyzed with the following form of the WLF equation(20):

$$\log_{10}\left(\frac{DT_0}{D_{T_0}T}\right) = \frac{c_1^D(T-T_0)}{c_2^D+T-T_0} \tag{7}$$

where $c_1^D = B_d / 2.303\, f(\phi_s)$, $c_2^D = f(\phi_s) / \alpha(\phi_s)$, $f(\phi_s)$ is the fractional free volume of the solution at the reference temperature T_0, ϕ_s is the volume fraction of toluene in PIB and $\alpha(\phi_s)$ is the fractional free volume expansion factor and D_{T_0} is the self diffusion coefficient at T_0. Equation (7) can be rewritten as:

$$\ln\left(\frac{DT_0}{D_{T_0}T}\right) = \frac{\frac{\alpha(\phi_s)}{B_d}(T-T_0)}{\frac{f(\phi_s)}{B_d}\left(\frac{f(\phi_s)}{B_d}+\frac{\alpha(\phi_s)}{B_d}(T-T_0)\right)} \tag{7a}$$

The parameters that were floated in order to fit the data were $\alpha(\phi_s) / B_d$ and $f(\phi_s) / B_d$. B_d is analogous to the B in equation (1) and will be defined precisely later. The fits along with the experimental self - diffusion coefficients at different concentrations and temperatures, are shown in Figure 1, and the reference temperature T_0 was chosen to be 298 K. The parameters obtained are shown in Table 1. After $\alpha(\phi_s)/B_d$ and $f(\phi_s)/B_d$ were obtained, the WLF coefficients c_1^D and c_2^D were calculated (from $c_1^D = B_d / 2.303\, f(\phi_s)$ and $c_2^D = f(\phi_s) / \alpha(\phi_s)$) and they are also shown in Table 1.

To fit the data at a constant temperature, as a function of concentration, the Fujita free volume theory(12) was first applied. As mentioned above, the theory begins with the result of Doolittle(16 - 18) who showed that the viscosity η of ordinary liquids of low molecular weight is given by equation (1).

To relate this to diffusion, the mobility, m, of a molecule is considered to be the velocity with which a molecule translates under the action of unit force and is inversely proportional to the molecular friction coefficient and the viscosity η (Stokes law). Thus equation (1) can be written as:

$$\ln(m) = A - B_d / f \tag{8}$$

Where B_d is the value of B for the minimum hole which is needed to allow a given molecule to undergo such a displacement(12,19) and is considered to be a measure of hole size. The definition of mobility in terms of the self - diffusion coefficient of a penetrant in a polymer matrix is(24):

$$D = RTm \tag{9}$$

where R is the gas constant, T is the absolute temperature and D is the self - diffusion coefficient.

In general the free volume of a given polymer - penetrant solution depends on temperature and concentration and it is more appropriate to denote the fractional free volume as $f(T, \phi_s)$ where again ϕ_s is the volume fraction of the penetrant. It has been shown$^{(25)}$ that if the increase in free volume by the addition of the diluent is proportional to the volume of the added penetrant, then:

$$v_f = (v_f)_2 + \gamma(T)\, v_1 \qquad (10)$$

$$v = v_1 + v_2 \qquad (11)$$

where v_f is the average free volume of the solution, $(v_f)_2$ is the average free volume of the pure polymer, $\gamma(T)$ is a proportionality factor that may be compared with the fractional free volume of the diluent, v is the total volume of the solution, v_1 is the volume of the penetrant and v_2 is the volume of the amorphous polymer. By dividing equation (10) with equation (11) the fractional free volume of the solution $f(T, \phi_s)$ is found to be a linear function of the volume fraction of the penetrant ϕ_s:

$$f(T, \phi_s) = f_p(T, 0) + (\, f_s(T) - f_p(T, 0)\,)\, \phi_s \qquad (12)$$

where $f_p(T, 0)$ is the fractional free volume of pure polymer and $f_s(T)$ is a parameter that represents the fractional free volume of the solvent trapped in the polymer matrix. $f_s(T) - f_p(T, 0)$ represents the effectiveness of the penetrant for increasing the free volume when it is dispersed in the given polymer. Equation (12) can be rewritten as:

$$\frac{f(T,\phi_s)}{B_d} = \frac{f_p(T)}{B_d} + \left(\frac{f_s(T)}{B_d} - \frac{f_p(T)}{B_d}\right)\phi_s \qquad (13)$$

If equations (12) and (8) are substituted into equation (9) considering that as $\phi_s \to 0$, $D \to D_0$ we obtain:

$$\ln\frac{D}{D_0} = \frac{B_d(f_s - f_p)\phi_s}{f_p^2 + (f_s - f_p)f_p\phi_s} = \frac{[(\frac{f_s}{B_d}) - (\frac{f_p}{B_d})]\phi_s}{(\frac{f_p}{B_d})^2 + [(\frac{f_s}{B_d}) - (\frac{f_p}{B_d})](\frac{f_p}{B_d})\phi_s} \qquad (14)$$

where ϕ_s is the penetrant volume fraction, D_0 is the diffusion coefficient of toluene at the limit of zero penetrant concentration, f_p is the average fractional free volume of pure polymer and f_s is the fractional free volume of toluene in the solution.

For each temperature, the diffusion coefficient of toluene as a function of concentration was fitted using equation (14). The parameters varied are D_0, (f_p / B_d) and (f_s / B_d). The reason for using (f_p / B_d) and (f_s / B_d) as fitting parameters and not f_p and f_s is to avoid making any assumptions about the parameter B_d. The parameters (f_p / B_d) and (f_s / B_d) do not have physical significance whereas f_p, f_s and B_d do. The parameters produced by the fit are shown in Table 2 and the lines corresponding to the fit in Figures 2 and 3.

From the diffusion coefficient of toluene at the limit of zero penetrant concentration in Table 2 and the WLF equation (7), WLF parameters can be obtained similar to those shown in Table 1. Those are shown in the Table 3 .

The self - diffusion of toluene in PIB was also analysed via the Vrentas - Duda theory(13-15,26-28). According to this theory the self diffusion coefficient of a penetrant into a rubbery polymer is given by:

$$D_1 = D_0 \exp\left(\frac{-E}{RT}\right) \exp\left[\frac{-(\omega_1 V_1^* + \omega_2 \xi V_2^*)}{\omega_1\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T) + \omega_2\left(\frac{K_{12}}{\gamma}\right)(K_{22} - T_{g2} + T)}\right] \quad (15)$$

where V_i^* is the specific critical hole free volume of component i required for a jump (i can be equal to 1 or 2; 1 for penetrant or solvent and 2 for polymer), ω_i is the mass fraction of component i, T_{gi} is the glass transition temperature of component i, D_0 is a constant pre-exponential factor, E is the energy per mole that a molecule needs to overcome attractive forces which constrain it to its neighbors and γ is an overlap factor (between 1/2 and 1) which is introduced because the same free volume is available to more than one molecule. K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are free volume parameters for the polymer.

The free volume parameters K_{11}, K_{21}, K_{12}, K_{22} are defined as follows(13):

$$K_{11} = V_1^0(T_{g1})[\alpha_1 - (1 - f_{H1}^G)\alpha_{c1}] \quad (16)$$

$$K_{21} = \frac{f_{H1}^G}{\alpha_1 - (1 - f_{H1}^G)\alpha_{c1}} \quad (17)$$

$$K_{12} = V_2^0(T_{g2})[\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}] \quad (18)$$

$$K_{22} = \frac{f_{H2}^G}{\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}} \quad (19)$$

$$f_{H1}^{G} = \frac{K_{11}K_{21}}{V_1^0(T_{g1})} \tag{20}$$

$$f_{H2}^{G} = \frac{K_{12}K_{22}}{V_2^0(T_{g2})} \tag{21}$$

where α_i is the thermal expansion coefficient for the equilibrium liquid component i, α_{ci} is the thermal expansion coefficient for the component i for the sum of the specific occupied volume and the specific interstitial volume, V_i^0 is the specific volume of the pure equilibrium component i and f_{Hi}^G is the fractional hole free volume of the component i at T_{gi}. Finally, ξ is the ratio of molar volume of a solvent jumping unit to the molar volume of a polymer jumping unit. The parameter ξ can be a measure of the molar volume of the polymer jumping unit when the entire solvent molecule performs a jump during the process of the self - diffusion.

There are nine independent parameters in equation (15), D_0, E, ξ, K_{11}/γ, $K_{21} - T_{g1}$, K_{12}/γ, $K_{22} - T_{g2}$, V_1^*, V_2^* that need to be determined. However, most of them can be determined from viscosity data or sources other than diffusion data and in favorable cases all of them could conceivably be set from other data. In order to fit the diffusion data of toluene in PIB as a function of concentration, the parameters shown in Table 4 were used. This parameter set was chosen from a number of literature sources and is discussed in some detail elsewhere[29]. Since all the toluene and polymer free volume parameters mentioned above are close to each other, the actual choice of a parameter set is somewhat arbitrary and doesn't significantly change the quality of the fit. As a result of the fit, ξ, the only parameter floated, was found to be equal to 0.892 ± 0.08. The experimental self - diffusion coefficients of toluene in PIB along with the fitting curves (solid lines) are shown as a function of temperature and concentration in Figures 4(a) and 4(b).

The polymer segmental motion was characterized using the ^{13}C T_1 data from the methylene carbon of PIB and applying the model based on the Hall-Helfand description[30] of segmental motion combined with restricted anisotropic rotational diffusion[2,31]. The equations that relate the spectral density function corresponding to this motional model and the spin - lattice relaxation time are given by:

$$\frac{1}{T_1} = W_0 + 2W_{1C} + W_2 \tag{22}$$

where

$$W_0 = \sum_j \gamma_C^2 \gamma_H^2 \hbar^2 \frac{J_0(\omega_H - \omega_C)}{20 r_j^6}$$

$$W_{1C} = \sum_j 3\gamma_C^2 \gamma_H^2 \hbar^2 \frac{J_1(\omega_C)}{40 r_j^6}$$

$$W_2 = \sum_j 3\gamma_C^2 \gamma_H^2 \hbar^2 \frac{J_2(\omega_H + \omega_C)}{10 r_j^6}$$

The methylene C - H distance is set at 1.09 Å. The expression for the spectral density function is described in detail elsewhere[2,29]. According to this model two correlation times describe the segmental motion of the polymer. One of them is τ_0 which is the correlation time for single conformational transitions and the other is τ_1 the correlation time for cooperative or correlated transitions. Each of these two correlation times was given an Arrhenius temperature dependence with activation energy E_{a0} and E_{a1} respectively and corresponding prefactors τ_∞. Also ℓ is the amplitude over which restricted rotational diffusion occurs and D_{ir} is the rotational diffusion constant. The form of the temperature dependence of ℓ and D_{ir} is shown below:

$$\ell = A\, T^{0.5} \text{ deg} \qquad (23)$$

$$D_{ir} = B\, T - C \text{ sec}^{-1} \qquad (24)$$

The results of fitting the T_1 field, temperature and concentration dependence is shown for a typical case in Figure 5 and the results are shown in Table 5 while the rest of the parameters have the values:

$$(\tau_\infty)_0 = 2.1\ 10^{-14} \text{ sec}; \quad (\tau_\infty)_1 = 1.0\ 10^{-14} \text{ sec} \qquad (25)$$

$$\ell = 5.15\, T^{0.5} \text{ deg}; \qquad D_{ir} = 3.26\ 10^{7}\, T - 3.5\ 10^{9} \text{ sec}^{-1} \qquad (26)$$

When a WLF temperature dependence was given to the correlation times, there are six parameters to be established: $(\tau_0)_0$, $(\tau_1)_0$, ℓ, D_{ir}, $c_1{}^0$ and $c_2{}^0$ ($c_1{}^0$ and $c_2{}^0$ are the WLF coefficients). The reference temperature was chosen to be $T_0 = 298$ K and accordingly:

$$\ln \frac{\tau_0}{(\tau_0)_0} = \frac{-2.303 c_1^0 (T - T_0)}{c_2^0 + T - T_0} \qquad (27)$$

$$\ln \frac{\tau_1}{(\tau_1)_0} = \frac{-2.303 c_1^0 (T - T_0)}{c_2^0 + T - T_0} \qquad (28)$$

$$c_1^0 = \frac{B_0}{2.303 f(\phi_s)} \tag{29}$$

$$c_2^0 = \frac{f(\phi_s)}{\alpha} \tag{30}$$

where $f(\phi_S)$ is the fractional free volume of the solution and α is the thermal expansion coefficient of the fractional free volume. B_0 represents the minimum void size necessary for a conformational transition. Comparable fittings to those obtained using the Arrhenius depedence are obtained and the fitting parameters are given in Table 6. Good agreement is evident for the fractional free volume of the solution derived from equation 29 and those values obtained from penetrant self diffusion analysis shown in Table 1.

There is no field strength dependence in the T_1 data for the ortho carbon of toluene. Therefore, the extreme narrowing limit equation is used for the interpretation:

$$\frac{1}{T_1} = \frac{4}{3}\gamma_H^2\gamma_C^2\hbar^2 S(S+1)\tau\frac{1}{r_{CH}^6} \tag{31}$$

where $S = 1/2$, τ is the correlation time for molecular tumbling and $r_{CH} = 1.08$ Å is the distance between the proton and the carbon on the toluene phenyl ring.

Again, at first an Arrhenius temperature dependence was given to the correlation time, where E is the activation energy for rotation and τ_∞ is a prefactor. Two parameters were floated E and τ_∞. During the fitting procedure it was found that τ_∞ is around $1.0\text{x}10^{-14}$ sec and changes little as a function of concentration. Thus the value of τ_∞ was set equal to $1.0\ 10^{-14}$ sec and E was the only parameter that was floated as concentration changed. The parameters obtained are shown in Table 7.

Next a WLF temperature dependence was assigned to the correlation time

$$\ln\frac{\tau}{\tau_0} = \frac{-2.303 c_1^0 (T - T_0)}{c_2^0 + T - T_0} \tag{32}$$

where τ_0 is the value of the correlation time τ at the reference temperature T_0 which again was chosen to be 298 K. $c_1{}^0$ and $c_2{}^0$ are the WLF coefficients at the reference temperature:

$$c_1^0 = \frac{B}{2.303 f(\phi_s)} \tag{33}$$

$$c_2^0 = \frac{f(\phi_s)}{\alpha} \qquad (34)$$

where $f(\phi_s)$ is the fractional free volume of the solution and α is the thermal expansion coefficient of the fractional free volume of the solution. B represents the minimal void size necessary for rotation. For the fitting process of the T_1 data $c_2{}^0$ was set equal to $c_2{}^D$ the WLF coefficient obtained from the temperature dependence of the self - diffusion of toluene in PIB - toluene solutions (Table 1). The parameters that were floated in order to fit the data are $c_1{}^0$ and τ_0. the values obtained are shown in Table 8. The fittings obtained are comparable to those obtained for the Arrhenius temperature dependence.

Discussion

It is clear that the self-diffusion of toluene in PIB is well described by free volume theories. Some comparisons between the different free volume treatments and the potential correlation between penetrant diffusion and polymer segmental motion can now be explored with the data in hand.

As a first step a comparison can be made between the fractional free volume determined from the temperature dependence of the translational diffusion of the toluene with that determined from the concentration dependence of the same quantity. Such a comparison is made in Figure 6 where the fractional free volume of the solution, $f(T, \phi_s)$, is presented as a function of the volume fraction of toluene in PIB. The points come from Table 1 and they were obtained from the WLF equation (7) where the temperature dependence of the toluene self - diffusion was analyzed, except the filled circle that represents the fractional free volume of pure toluene (at 293 K) obtained from viscosity data(32). The solid line was obtained from equation (13) using the values of Table 2 for $f_p(T)$ and $f_s(T)$ (obtained from equation (14) where the concentration dependence of the toluene self - diffusion was analyzed). The error bars represent an uncertainty of approximately 20% for $f(T, \phi_s)$ in Table 1, which comes from quality of the fitting (namely the fitting of the temperature dependence of the self - diffusion of toluene in PIB). As can be seen from Figure 6, the values of the fractional free volume of the solution that are obtained from the analysis of the temperature and concentration dependencies of the self - diffusion of toluene in PIB, are, in fact, close to each other.

A free volume analysis of the viscosity of the toluene - PIB solution was done by Fujita(32). In that study the fractional free volume of the solution, $f(293\text{ K}, \phi_s)$, and the fractional free volume of toluene trapped in the polymer matrix, $f_s(293\text{ K})$, are reported as a function of concentration at 293 K. The fractional free volumes of the solutions at 293 K obtained from the self - diffusion data are in reasonable agreement with the values obtained from the viscosity data[32]. This establishes the utility of the free volume approach in relation to molecular mobility of a penetrant in a polymer. Viscosity is macroscopic measure, while the diffusion measurements presented here are microscopic measurements looking specifically at the penetrant molecule. Two different experiments probing two different levels of dynamics give approximately the same fractional free volume for the solutions, when the appropriate value for the minimum void size necessary for diffusion relative to viscosity was chosen.

Another result that has been confirmed, is the decrease of the fractional free volume of toluene when the latter is trapped in entangled PIB. This is seen by direct comparison between the free volume of toluene trapped in PIB (Table 2) and the data for neat toluene from viscosity data[12,32] The same conclusion has been reached from the viscosity data(32), with a completely different approach. Also the fractional free volume parameters for pure PIB obtained from this work are similar to the values reported in the literature and extracted from other diffusion or viscoelastic measurements. This confirms the correctness of the magnitude of the free volume of the particular polymer.From the preceding it is obvious that B_d, the parameter that represents the minimum void size necessary for a penetrant molecule to diffuse, is important if results obtained from different methods that observe different kind of motions are to be compared. This is to be expected since the size of a moving unit is not the same for different kind of motions. The unfortunate fact is that it is not possible to obtain the dimension of the void when the parameter B_d is known.

The stated advantage of the Ventras-Duda theory is that the parameters can be independently determined and the theory has potential predictive capability. In our use of Ventras-Duda the only fitting parameter is ξ, the ratio of the molar volume of solvent jumping unit to the molar volume of polymer jumping unit, given by:

$$\xi = \frac{V_1^0(0)}{V_{2j}} = \frac{M_1 V_1^*}{M_{2j} V_2^*} \qquad (35)$$

The value determined for ξ of 0.892 ± 0.08. corresponds to a polymer jumping unit of molecular weight 94.3 as derived from equation (35) when the toluene moves as a single unit. This value is close to the molecular weight of toluene ($M_1 = 92.13$). It is thus seen that the size of the polymer jumping unit is approximately the same as the size of the penetrant jumping unit. In view of this result, it would be appropriate to expect that both polymer and penetrant jumping units would require approximately the same minimum hole size necessary for a diffusion jump. It has been shown(13) previously that both Fujita and Vrentas - Duda free volume theories can be used when the molecular weights of the two jumping units are the same. As indicated in reference (33), the two theories are identical when the following condition is true:

$$\frac{\xi V_2^*}{V_2^0} = \frac{V_1^*}{V_1^0} \tag{36}$$

and when B_d (minimum hole size required for a given molecule to permit a displacement, according to Fujita theory[12]) is defined as:

$$B_d = \frac{\gamma V_1^*}{V_1^0} \tag{37}$$

This can be shown by rewriting equation (15) as:

$$\ln\left(\frac{D_1}{D_1(0)}\right) = \frac{\phi_1\left(\frac{\xi V_2^* f_1}{V_2^0 \gamma} - \frac{V_1^* f_2}{V_1^0 \gamma}\right)}{\left[\frac{f_2^2}{\gamma^2} + \phi_1 \frac{f_2}{\gamma}\left(\frac{f_1}{\gamma} - \frac{f_2}{\gamma}\right)\right]} \tag{38}$$

where $D_1(0)$ is the self - diffusion coefficient of the penetrant at the limit $\omega_1 = 0$, V_i^0 is the specific volume of pure component i at the temperature of interest, V_i^* is the specific critical hole free volume of component i required for a jump, ϕ_1 is the volume fraction of the solvent and f_i is the fractional hole - free volume of pure component i at the temperature of interest and the f_i's are given by:

$$f_1 = \frac{(K_{21} + T - T_{g1})K_{11}}{V_1^0} \qquad f_2 = \frac{(K_{22} + T - T_{g2})K_{12}}{V_2^0} \tag{39}$$

Using equations (36) and (37), equation (38) can be written as:

$$\ln\left(\frac{D_1}{D_1(0)}\right) = \frac{B_d(f_1 - f_2)\phi_1}{f_2^2 + f_2(f_1 - f_2)\phi_1} \tag{40}$$

Equation (40) is identical to the equation derived by Fujita(12). For $\xi = 0.892$, $V_2^* = 1.004$ cm^3 / gr, $V_1^* = 0.917$ cm^3 / gr, $V_2^0 = 1.091$ cm^3 / gr, and $V_1^0 = 1.154$ cm^3 / gr we find that the left hand side of equation (36) is equal to 0.821 and the right hand side of equation (36) is equal to 0.794. Therefore we see that since the two ratios are close, either of the two theories can be used for the toluene - polyisobutylene system. Thus it is no surprise that both approaches accurately describe the temperature and concentration dependence of the self - diffusion constant.

It would be desirable if the ideas from these free volume concepts were able to shed some light on the rather unique behaviour of PIB relative to other polymers. In particular the unusual slow diffusion exhibited by PIB with respect to a variety of penetrants might be expected to be reflected in the value of certain free volume parameters. This is seen in the fact that the WLF parameters: c_1 and c_2, are considerably different from most other polymers, which can be adequately represented by the so-called universal values. The parameter α, the fractional free volume expansion factor, is considerably smaller than is typical for other polymers and does give some physical insight into the origin of the lower free volume at temperatures above the glass transition. This parameter is derived directly from the Fujita analysis. The Vrentas-Duda parameters, though useful in their potential for predictability, do not appear to yield any physical insight into uniqueness of PIB.

If we now include consideration of the relaxation data, three different kind of motions were considered: the self - diffusion of toluene in high molecular weight PIB, the molecular rotation of toluene and the segmental motion of the polymer. In general the c_1^0 WLF coefficient obtained from these three types of motion should be different, because of the different hole sizes required for each type of motion to occur, i.e., B's (in general $c_1^0 = B/2.303f(\phi_s)$ and $c_2^0 = f(\phi_s) / \alpha$). For the case of diffusion we have B_d, for the toluene rotation B and for the segmental motion of the polymer B_0.

In Table 9, $(f(\phi_s) / B_0)$ obtained from segmental motion and $(f(\phi_s) / B_d)$ obtained from translational diffusion are compared. From Table 9, it can be seen that the two parameters are close to each other, considering their uncertainties: of the order of ± 0.015 at low concentration, up to ± 0.05 at high toluene concentrations. The agreement is very good noting that the values are extracted by different methods from two completely different sets of data that describe different components of the solution. The toluene self - diffusion data were collected by observing directly the toluene molecule and the T_1 data were collected by observing the methylene carbon of PIB in the toluene - PIB solutions. From Table 9, since the fractional free volume of the solution, $f(\phi_s)$ and the thermal expansion coefficient of the free volume, α, are unique and independent of the type of motion that is examined, it can be concluded that $B_d \approx B_0$. Also the value of ξ, obtained from the Vrentas - Duda theory is 0.892 which corresponds to a polymer jumping unit with molecular weight 94.3. This is very nearly equal to the molecular weight of toluene which is 92. The fact that the two nearly coincide with each other means that the two jumping units will need the same minimal free volume for translation (for toluene) and a conformational transition (for the polymer) implying that B_d should equal B_0.

Another way to check to see if the two motions are correlated, is to directly compare the correlation time for translational diffusion τ_D and the correlation time for segmental motion (correlation time for single conformational transition). The first can be obtained from(34):

$$\tau_D = \frac{b^2}{D} \tag{41}$$

where D is the self - diffusion coefficient of toluene, b is the distance of closest approach which is between 2.2 Å - 3.3 Å. Using 2.7 Å as the distance of closest approach and the self - diffusion of toluene in PIB - toluene solution, the correlation time for translational diffusion is calculated and shown in Table 10 The correlation time for a conformational transition, τ_0, is calculated from the Arrhenius equation and also shown in Table 10 It can be seen that the two correlation times are in agreement at the 0.045 toluene volume fraction which means at this low penetrant concentration the two motions (segmental and translational diffusion) are correlated. As we go to higher concentrations the difference between the τ_0 correlation time and the τ_D becomes larger up to two orders of magnitude at 0.712 toluene volume fraction. This might be expected since as we go towards higher concentrations a toluene molecule has fewer polymer molecules in its neighbourhood and it is not necessary for a polymer segment to move in order a toluene molecule to translate.

Thus we see that the two processes (diffusion and conformational transition) require similar minimum free volumes in order to occur and the time scale of the two motions are correlated at low concentrations of penetrant.

The spin - lattice relaxation data on the ortho carbon of toluene do not provide as much information about the motion of toluene as the corresponding data on PIB. However, at all concentrations the correlation time for toluene reorientation is two or more orders of magnitude faster than segmental motion and translational diffusion. Thus the reorientational motion of the toluene is uncoupled from the other two motions. The WLF analysis of the temperature dependence also leads to different values of c_1^0 and thus B further supporting the separation of these motions. Toluene reorientation would appear to be a much more rapid motion involving a smaller hole size.

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Table 1

Parameters obtained from the temperature dependence fit of the toluene self - diffusion coefficient, using equation (6).

ϕ_s	$f(\phi_s) / B_d$	$\alpha(\phi_s) / B_d$ (deg^{-1})	c_1^D	c_2^D (K)
0.045	0.0904	$5.83\ 10^{-4}$	4.803	155.060
0.104	0.1050	$6.84\ 10^{-4}$	4.135	153.509
0.205	0.1270	$7.25\ 10^{-4}$	3.419	175.172
0.327	0.1550	$8.44\ 10^{-4}$	2.801	183.649
0.409	0.1900	$9.60\ 10^{-4}$	2.285	197.917
0.712	0.2700	$1.10\ 10^{-3}$	1.608	245.455
1.000	0.3700	$1.70\ 10^{-3}$	1.174	217.647

Table 2

Parameters obtained from the concentration dependence fit of the toluene self - diffusion coefficient, using equation (14).

T(K)	f_s / B_d	f_p / B_d	D_0 (cm^2 / sec)
298	0.273	0.08735	$9.08\ 10^{-9}$
310	0.300	0.09780	$2.55\ 10^{-8}$
320	0.333	0.10700	$5.15\ 10^{-8}$
329	0.364	0.11630	$8.70\ 10^{-8}$
339	0.381	0.12500	$1.55\ 10^{-7}$
349	0.398	0.13200	$2.30\ 10^{-7}$
358	0.423	0.14100	$3.40\ 10^{-7}$
368	0.449	0.14450	$4.10\ 10^{-7}$

Table 3

Parameters obtained from the temperature dependence fit of the toluene self - diffusion coefficient at zero toluene concentration (D_0, shown in Table 2), using equation (7).

ϕ_s	$f(\phi_s) / B_d$	$\alpha(\phi_s) / B_d$ (deg^{-1})	c_1^D	c_2^D (K)
0.000	0.0818	$5.34\ 10^{-4}$	5.308	153.184

Table 4

Values of parameters for PIB / Toluene systems.

V_1^* (cm^3 / gr)	0.917
V_2^* (cm^3 / gr)	1.004
K_{11} / γ (cm^3 / gr K)	1.45 10^{-3}
K_{12} / γ (cm^3 / gr K)	4.351 10^{-4}
$K_{21} - T_{g1}$ (K)	-86.32
$K_{22} - T_{g2}$ (K)	-97.6
ξ	0.892 ± 0.08
D_0 (cm^2 / sec)	4.82 10^{-4}
E (kcal / mole)	0
M_1	92.13
V_1^0 (cm^3 / gr mole)	84.48
T_{g1} (K)	117
M_{2mono}	56.04
C_{12}^g	9.33
C_{22}^g (K)	107.4
T_{g2} (K)	205

Table 5

Activation energies for conformational transitions as a function of concentration of toluene in PIB.

Volume Fraction of toluene in PIB.	E_{a0} (kJ / mole)	E_{a1} (kJ / mole)
0.045	34.0	34.5
0.104	33.4	33.7
0.205	32.7	32.0
0.327	31.9	30.0
0.409	31.7	28.4
0.712	30.4	25.7

Table 6

Fitting parameters of the spin - lattice relaxation data when a WLF temperature dependence was given to the correlation times.

Volume Fraction of toluene in PIB	$(\tau_0)_0$ (sec)	$(\tau_1)_0$ (sec)	c_1^0	c_2^0 (K)
0.045	$3.00\ 10^{-8}$	$1.20\ 10^{-8}$	4.30	155.06
0.104	$1.80\ 10^{-8}$	$8.40\ 10^{-9}$	3.80	153.50
0.205	$8.85\ 10^{-9}$	$4.25\ 10^{-9}$	3.40	175.17
0.327	$6.23\ 10^{-9}$	$1.88\ 10^{-9}$	2.75	183.65
0.409	$3.40\ 10^{-9}$	$9.70\ 10^{-10}$	2.65	197.92
0.712	$3.00\ 10^{-9}$	$4.00\ 10^{-10}$	1.85	245.45

Table 7

Fitting parameters of the ortho carbon T_1 data when an Arrhenius temperature dependence was given to the correlation time.

Volume fraction of toluene in PIB ϕ_S	τ_∞ (sec)	E (kJ / mole)
0.045	$1.0\ 10^{-14}$	22.73
0.104	$1.0\ 10^{-14}$	21.84
0.205	$1.0\ 10^{-14}$	20.76
0.327	$1.0\ 10^{-14}$	18.50
0.409	$1.0\ 10^{-14}$	16.77
0.712	$1.0\ 10^{-14}$	14.00

Table 8

Fitting parameters of the ortho carbon T_1 data when a WLF temperature dependence was given to the correlation time.

Volume fraction of toluene in PIB ϕ_S	τ_0 (sec) at T_0 298K	$c_1{}^0$ at 298 K	$c_2{}^0$ (K) at 298 K
0.045	$9.72\ 10^{-11}$	2.45	155.06
0.104	$6.80\ 10^{-11}$	2.35	153.50
0.205	$4.10\ 10^{-11}$	2.25	175.17
0.327	$1.67\ 10^{-11}$	2.10	183.65
0.409	$8.40\ 10^{-12}$	2.00	197.92
0.712	$2.90\ 10^{-12}$	1.81	245.45

Table 9

Fractional free volume comparison of the PIB - toluene solutions obtained from the diffusion data analysis(17) and from the T_1 data presented in this work.

Volume fraction of toluene in PIB ϕ_s	$f(\phi_s) / B_d$ From Diffusion data	$f(\phi_s) / B_0$ From T_1 data
0.045	0.090	0.101
0.104	0.105	0.114
0.205	0.127	0.127
0.327	0.155	0.158
0.409	0.190	0.164
0.712	0.270	0.235

Table 10

Comparison of the correlation times for diffusion, τ_D, and for single conformational transitions τ_0 for 0.045 toluene volume fraction.

D (cm^2 / sec) Toluene Volume Fraction = 0.045	T (K)	τ_0 (sec)	τ_D (sec)
$2.55\ 10^{-8}$	298	$1.915\ 10^{-8}$	$2.859\ 10^{-8}$
$6.66\ 10^{-8}$	310	$1.126\ 10^{-8}$	$1.095\ 10^{-8}$
$1.26\ 10^{-7}$	320	$7.453\ 10^{-9}$	$5.786\ 10^{-9}$
$2.04\ 10^{-7}$	329	$5.254\ 10^{-9}$	$3.574\ 10^{-9}$
$3.11\ 10^{-7}$	339	$3.642\ 10^{-9}$	$2.344\ 10^{-9}$
$4.55\ 10^{-7}$	348	$2.666\ 10^{-9}$	$1.602\ 10^{-9}$
$6.31\ 10^{-7}$	357	$1.982\ 10^{-9}$	$1.155\ 10^{-9}$
$8.14\ 10^{-7}$	367	$1.451\ 10^{-9}$	$8.956\ 10^{-10}$

Figure Captions

Figure 1: Self - diffusion coefficient of toluene in PIB solutions as a function of temperature at different concentrations. The solid lines represent fits to the WLF diffusion equation presented in the text. The zero penetrant (0%) concentration points are from Table 2.

Figure 2: Self - diffusion coefficient of toluene in PIB solutions as a function of concentration at different temperatures. Solid lines represent fits to Fujita free volume theory presented in the text.

Figure 3: Self - diffusion coefficient of toluene in PIB solutions as a function of concentration at different temperatures. Solid lines represent fits to Fujita free volume theory presented in the text.

Figure 4(a) and 4(b): Diffusion coefficient of toluene in PIB as a function of concentration at different temperatures. Solid lines represent diffusion coefficients calculated from equation (15) of Ventras-Duda.

Figure 5: T_1 of the methylene carbon of PIB in toluene - PIB solutions as a function of temperature and Larmor frequency. The volume fraction of toluene in PIB is 0.045. An Arrhenius temperature dependence was given to the correlation times. The solid line corresponds to the fit for the Hall - Helfand function combined with anisotropic restricted rotational diffusion.

Figure 6: Comparison of the fractional free volume of the toluene - PIB solution, obtained from the temperature (points) and concentration (line) dependence of the diffusion coefficient. Solid line represents values obtained from equation (13). Filled circle represents the fractional free volume of pure toluene at 293 K(32).

fig1

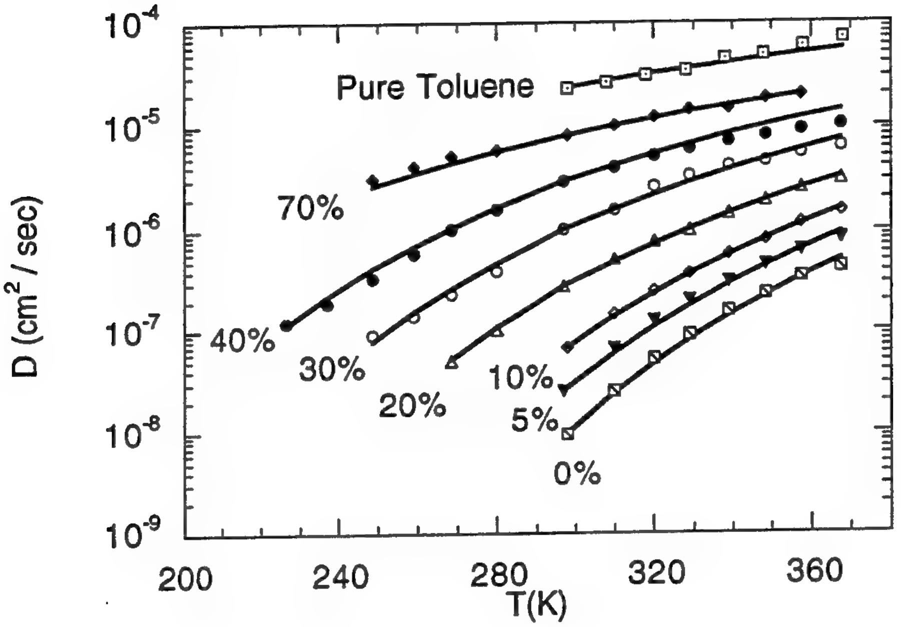

10^-4
10^-5
10^-6
10^-7
10^-8
10^-9
D (cm^2 / sec)
Pure Toluene
70%
40%
30%
20%
10%
5%
0%
200
240
280
320
360
T(K)

fig 2

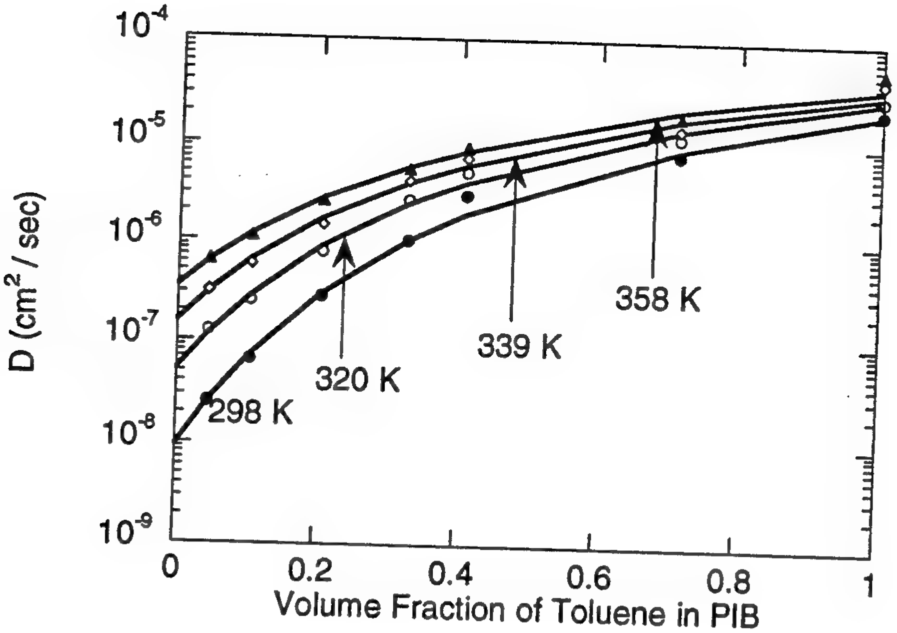

10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
D (cm^2 / sec)
358 K
339 K
320 K
298 K
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene in PIB

fig 3

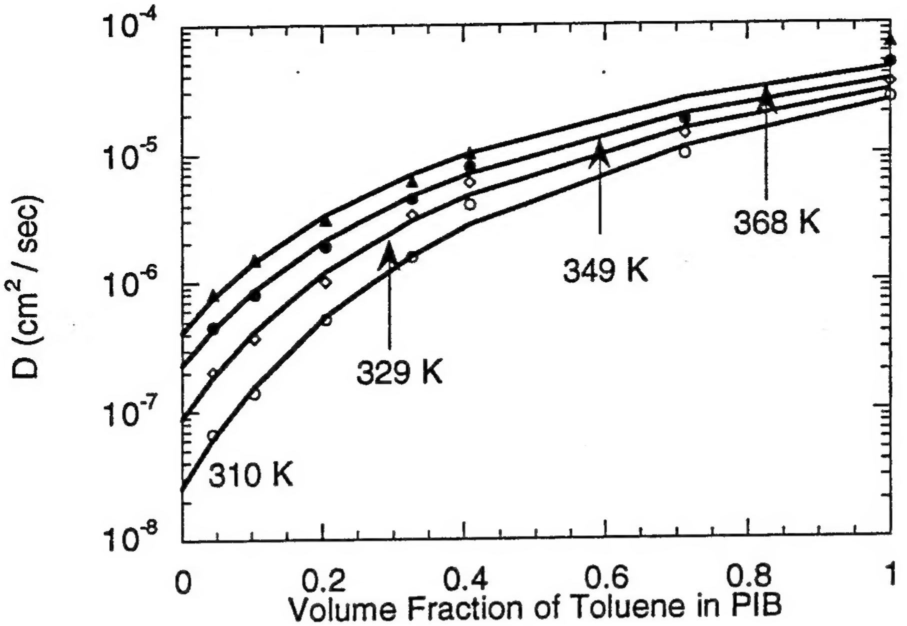

D (cm^2 / sec)
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene in PIB
310 K
329 K
349 K
368 K

fig 4a

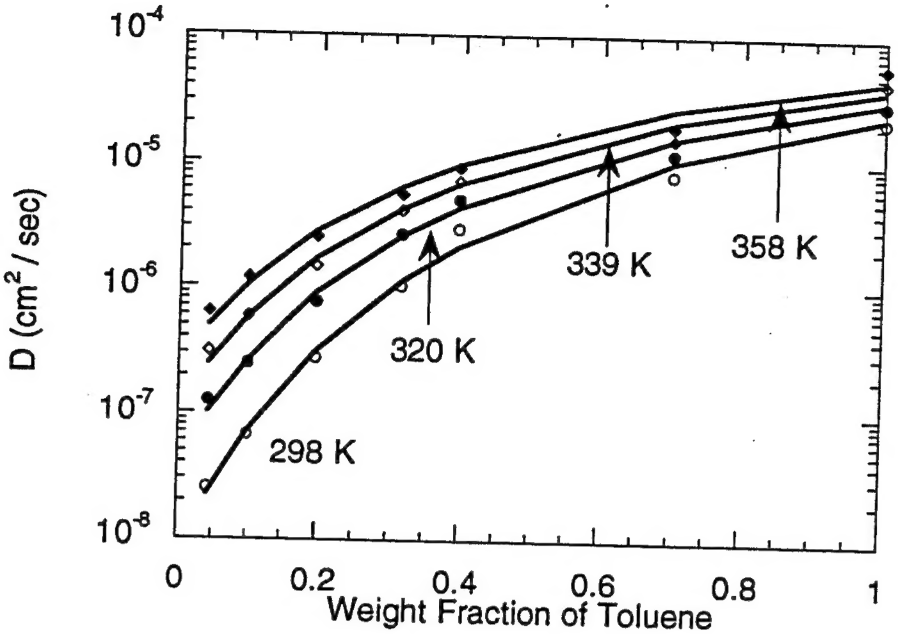

10^-4
10^-5
10^-6
10^-7
10^-8
D (cm^2 / sec)
0
0.2
0.4
0.6
0.8
1
Weight Fraction of Toluene
298 K
320 K
339 K
358 K

fig 4b

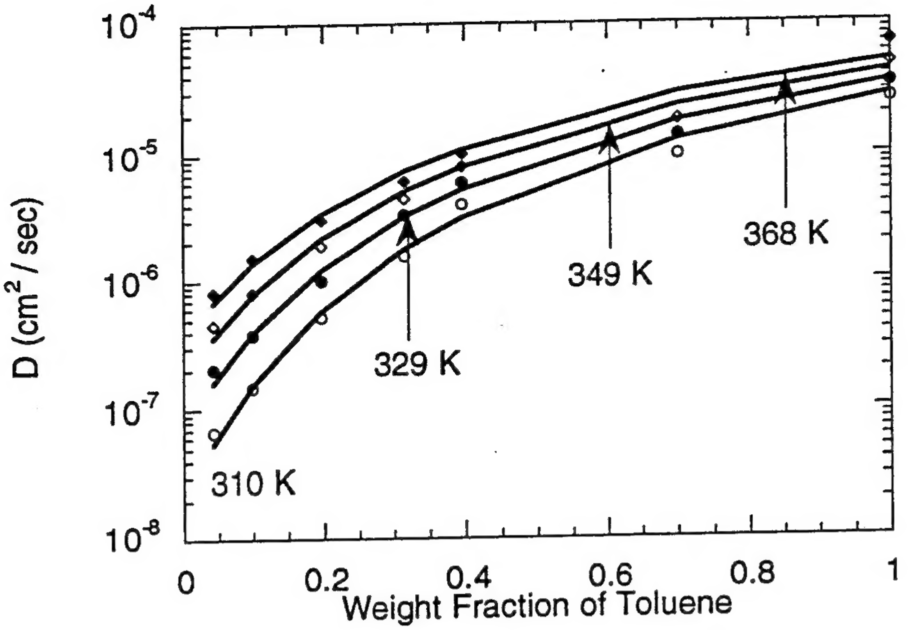

10^-4
10^-5
10^-6
10^-7
10^-8
D (cm² / sec)
0
0.2
0.4
0.6
0.8
1
Weight Fraction of Toluene
310 K
329 K
349 K
368 K

fig 5

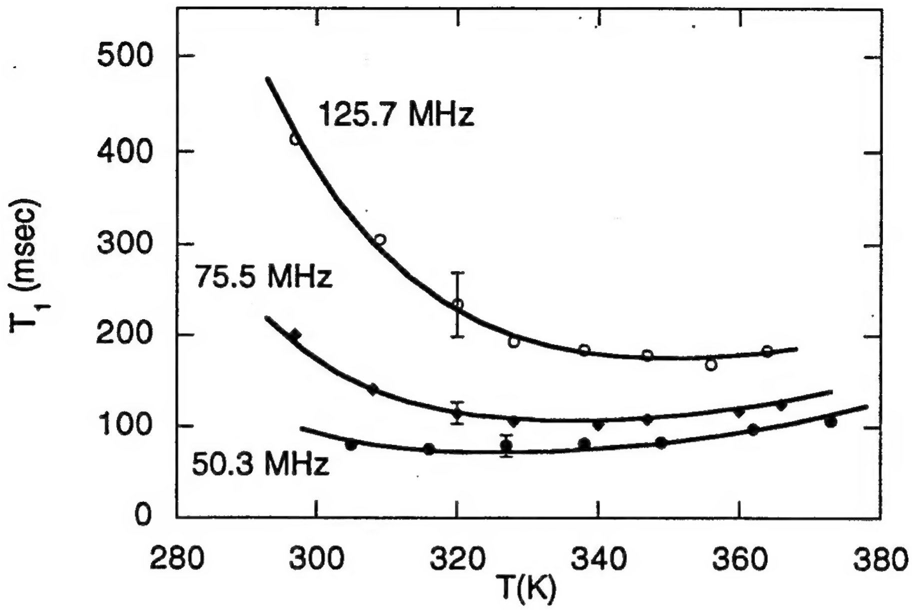
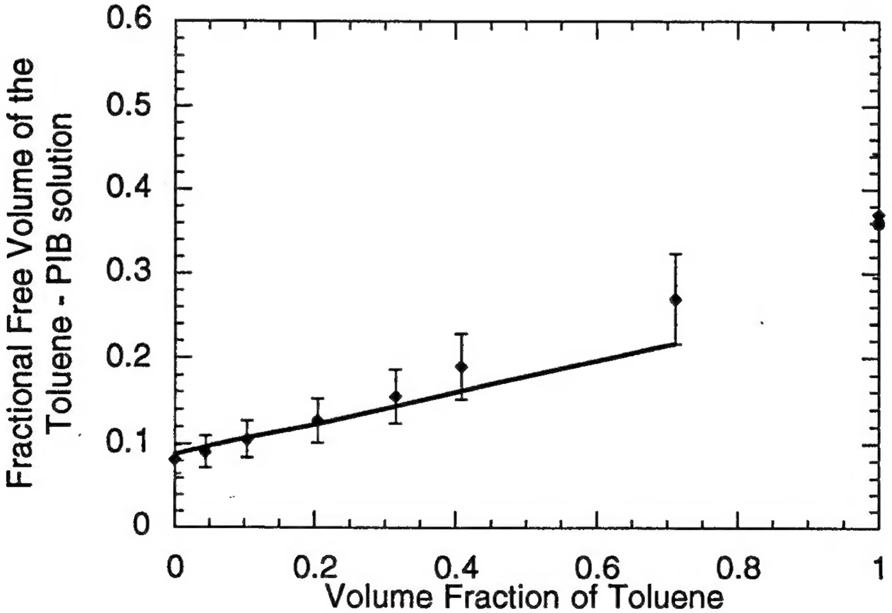

125.7 MHz
75.5 MHz
50.3 MHz
T_1 (msec)
500
400
300
200
100
0
280
300
320
340
360
380
T(K)

fig 6


Fractional Free Volume of the Toluene - PIB solution
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
Volume Fraction of Toluene